PB88-149059

Locating and Estimating Air Emissions from Sources of Polycyclic Organic Matter (POM)

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Sep 87

U.S. Department of Commerce
National Technical Information Service
NTIS

PB88-149059

United States
Environmental Protection
Agency

Air

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/4-84-007p
September 1987

EPA

Locating And Estimating Air Emissions From Sources Of Polycyclic Organic Matter (POM)

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-450/4-84-007p

2.

3. RECIPIENT'S ACCESSION NO.
PB88 149059/AS

4. TITLE AND SUBTITLE
Locating And Estimating Air Emissions From Sources Of
Polycyclic Organic Matter (POM)

5.
September 1987

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Office Of Air Quality Planning And Standards (MD 14)
U. S. Environmental Protection Agency
Research Triangle, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES
EPA Project Officer: Thomas F. Lahre

16. ABSTRACT

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this to compile available information on sources and emissions of these substances. This document deals specifically with polycyclical organic matter (POM). Its intended audience includes Federal, State and local air pollution personnel and others interested in locating potential emitters of POM and in making gross estimates of air emissions therefrom.

This document presents information on 1) the types of sources that may emit POM, 2) process variations and release points that may be expected within these sources, and 3) available emissions information indicating the potential for POM release into the air from each operation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
POM PAH PNA Polycyclic organic matter Polycyclic aromatic hydrocarbons Polynuclear aromatics Locating air emissions sources Toxic substances Benzo(a)pyrene		

18. DISTRIBUTION STATEMENT

19. SECURITY CLASS *(This Report)*

20. SECURITY CLASS *(This page)*

21. NO. OF PAGES
400

22. PRICE
PC$32.95/ MF 6.95

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-450/4-84-007p
September 1987

Locating And Estimating Air Emissions From Sources Of Polycyclic Organic Matter (POM)

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office Of Air And Radiation
Office Of Air Quality Planning And Standards
Research Triangle Park, North Carolina 27711

This report has been reviewed by the Office Of Air Quality Planning And Standards, U.S. Environmental Protection Agency, and has been approved for publication as received from the contractor. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, neither does mention of trade names or commercial products constitute endorsement or recommendation for use.

EPA-450/4-84-007p

TABLE OF CONTENTS

Section		Page
	List of Tables	v
	List of Figures	xi
1	Purpose of Document	1
2	Overview of Document Contents	3
3	Background	5
	Nature of Pollutant	5
	Nomenclature and Structure of Selected POMs	7
	Physical Properties of POM	7
	Chemical Properties of POM	13
	POM Formation Mechanisms in Combustion Sources	13
	Conversion of POM from Vapor to Particulate	19
	Persistence and Fate in the Atmosphere	23
	References for Section 3	29
4	POM Emission Source Categories	33
	Stationary Combustion of Solid, Liquid, and Gaseous Fuels for Heat and Power Generation	33
	Mobile Sources of POM	80
	Municipal, Industrial, and Commercial Waste Incineration	105
	Sewage Sludge Incineration	121
	Petroleum Catalytic Cracking - Catalyst Regeneration	135
	Sintering in the Iron and Steel Industry	153

Section Page

Ferroalloy Manufacturing 161

Iron and Steel Foundries 181

By-product Coke Production 186

Asphalt Roofing Manufacturing 204

Hot Mix Asphalt Production 221

Carbon Black Manufacture 236

Secondary Lead Smelting 253

Primary Aluminum Production 262

Wood Charcoal Production 272

Creosote Wood Treatment 283

Oil Shale Retorting 292

Asphalt Paving and Coal Tar Pitch and Asphalt Roofing Operations 304

Transfer and Handling of Coal Tar and Petroleum Pitch 311

Burning Coal Refuse Piles, Outcrops, and Mines 314

Prescribed Burning and Uncontrolled Forest Fires 321

Agricultural Burning 332

Miscellaneous Open Burning 337

References for Section 4 343

5 Source Test Procedures 359

Sample Collection Methods 359

Sample Recovery 371

Identification and Quantification of POM 376

References for Section 5 378

LIST OF TABLES

Table		Page
1	Physical Properties of Various POM Compounds	11
2	Percent of Total PAH Associated with Soot Particles as a Function of Temperature	22
3	Half Lives (in Hours) of Selected POM in Simulated Daylight, Subjected to Varying Concentrations of Atmospheric Oxidants (Ozone)	27
4	POM Emission Factors for Pulverized Coal Utility Boilers	44
5	POM Emission Factors for Coal-fired, Cyclone Utility Boilers	46
6	POM Emission Factors for Coal-fired, Stoker Utility Boilers	48
7	POM Emission Factors for Pulverized Coal Industrial Boilers	51
8	POM Emission Factors for Coal-fired, Stoker Industrial Boilers	52
9	Uncontrolled POM Emission Factors for Commercial and Residential Coal-fired Boilers	54
10	POM Emission Factors for Residual Oil Combustion	58
11	Uncontrolled POM Emission Factors for Distillate Oil Combustion	61
12	POM Emission Factors for Industrial and Commercial Wood-fired Boilers	62
13	POM Species Emission Factors for Controlled and Uncontrolled Wood-fired Industrial Boilers	64
14	Test Site Descriptions for the Emission Factors Given in Table 13	65
15	POM Emission Factors for Wood-fired Residential Heating Sources	68

Table Page

16 POM Emission Factors for Uncontrolled Wood-fired Heaters Under Various Burn Conditions 74

17 Uncontrolled POM Emission Factors for Natural Gas-fired Sources 75

18 POM Emission Factors for Bagasse-fired Industrial Boilers 77

19 Contributions of Various Mobile Source Categories to Total Mobile Source PAH and 1-Nitropyrene Emissions in 1979 83

20 Benzo(a)pyrene Emission Factors at Various Levels of Emission Control 85

21 Benzo(a)pyrene Emission Rates at Various Mileage Intervals 86

22 Change in Average POM Emissions with Deposit Condition and POM Content of Fuels 88

23 Estimated Particulate Benzo(a)pyrene Emission Factors for Gasoline Automobiles, Model Years 1966-1976 91

24 Measured and Derived POM Emission Factors for Mobile Sources 93

25 Average Emission Rates of Particulate POMs from Gasoline and Diesel Vehicles in Two Tunnels in Japan at an Average Speed of 50 mi/hr 94

26 Average Particulate POM Emission Rates for Gasoline Vehicles, Model Years 1970-1981, Under FTP and HWFET Test Cycles 95

27 Emission Rates of Particulates and Particulate POMs for Various Gasoline and Diesel Automobiles Under the FTP Test Cycle 98

28 POM Compounds Analyzed by HPLC-Fluorescence in Diesel Automobile Exhaust Particulates 99

29 Mean and Range of Concentrations of POMs in Exhaust Particulate from Four Diesel Cars 100

30 Particulate POM Emission Rates from a Turbocharged Mack Engine at Various Loads 102

Table Page

31 Total POM Emission Factors for the Ford Prototype Diesel Engine 103

32 POM Compounds Identified by GC/MS Analysis in Exhaust from a Gas Turbine Engine Burning Kerosene-type Fuel 106

33 POM Emission Factors for Municipal Waste Incinerators 117

34 Locations of Conventional Municipal Waste Incinerators in the United States 122

35 Locations of Modular Municipal Waste Incinerators in the United States 123

36 Distribution of Emission Control Technologies Applied to Selected Sewage Sludge Incinerators Prior to 1978 130

37 Distribution of Emission Control Technologies Applied to Selected Sewage Sludge Incinerators After 1978 131

38 POM Emission Factors for a Sewage Sludge Incinerator Controlled by a Wet Scrubber 133

39 POM Compounds Identified in Sewage Sludge Incinerator Emissions 134

40 Approximate Distribution of Sludge Combustion Facilities by State and Type in 1985 136

41 Locations of Wastewater Treatment Plants Thought to be Using Sewage Sludge Incinerators 138

42 POM Emission Factors for Petroleum Catalytic Cracking Catalyst Regeneration Units 152

43 Locations of Active Petroleum Refineries with Catalytic Crackers as of January 1986 154

44 Locations of Iron and Steel Industry Sinter Plants in 1977 162

45 Major Types of Ferroalloys Produced in the United States 164

46 POM Emission Factors for Electric Arc Furnaces Producing Ferroalloys 176

47 Locations of Ferroalloys Producers in the United States in 1984 178

Table Page

48 Emission Controls Used on POM Emission Sources in By-product Coke Plants 193

49 Specific POM Compounds Detected in Oven Door Leak Emissions 195

50 POM Compounds Detected in Battery Topside Emissions 196

51 Specific POM Compounds Detected in Quench Tower Emissions 197

52 POM Emission Factor Data for Slot Oven Coking Sources 199

53 POM Emission Factor Data for Coke By-product Recovery Processes 200

54 Locations of By-product Recovery Process Coke Production Plants in the United States in 1984 201

55 Control Devices Used on POM Emission Sources in Asphalt Roofing Plants 217

56 Summary of POM Emission Factor Data for Sources in Asphalt Roofing Material Plants 218

57 Asphalt Roofing Manufacturing Locations in the United States in 1986 222

58 Production Capacity Distribution for Batch, Continuous, and Drum-mix Hot Mix Asphalt Plants 225

59 POM Emission Factors for Hot Mix Asphalt Plants 235

60 Individual POM Species Emission Factors for a Drum-mix Hot Mix Asphalt Plant Using Virgin Feed Material 237

61 Individual POM Species Emission Factors for a Drum-mix Hot Mix Asphalt Plant Using Recycled Feed Material 238

62 Individual POM Species Emission Factors for a Batch-mix Hot Mix Asphalt Plant Using Virgin Feed Material 239

63 Stream Code for the Oil Furnace Process Illustrated in Figure 28 242

64 Individual POM Compounds Measured in the Test of an Oil-furnace Carbon Black Plant 248

Table Page

65 Summary of POM Emission Factors for Oil-furnace Carbon Black Plants 250

66 Locations and Annual Capacities of Carbon Black Producers in 1985 251

67 POM Concentrations in Stack Gases of a Secondary Lead Smelter 261

68 Secondary Lead Smelters in the United States in 1985 263

69 POM Emission Factors for Primary Aluminum Smelting Plants 271

70 POM Compounds Identified in the Emissions of a Primary Aluminum Smelter 273

71 List of Primary Aluminum Production Facilities in the United States in 1985 275

72 Charcoal Producers in the United States 284

73 List of Creosote Wood Impregnation Plants in the United States 293

74 POM Concentrations Measured in Air Around Asphalt Paving Operations 307

75 POM Concentrations Released from Freshly Paved Asphalt Exposed to Light 309

76 POM Concentrations from Freshly Paved Asphalt Under Differing Light and Humidity Conditions 310

77 POM Concentrations Associated with Asphalt and Coal Tar Pitch Roofing Operations 312

78 Burning Coal Refuse Piles, Impoundments, Abandoned Mines, and Outcrops in the United States by State 322

79 Particulate POM Emission Factors from Burning Pine Needles by Fire Type 329

80 Particulate POM Emission Factors from Burning Pine Needles by Fire Phases - Heading Fire 330

81 Total POM and Benzo(a)pyrene Emission Factors from Burning Pine Needles as a Function of Total Suspended Particulate Matter Emissions 331

Table Page

82 Distribution of Prescribed Burning in the United States in 1984 333

83 POM Emission Factors for Open Burning as a Function of Total Particulate Matter Emissions 339

84 POM Emission Factors for Open Burning as a Function of the Amount of Waste Burned 340

85 POM Emission Factors for the Open Burning of Municipal Refuse, Automobiles, and Landscaping Refuse 341

86 Comparison of Modified Method 5 Train/SASS Characteristics 361

87 Distribution of POM in the Particulate and Gas Phase from Vehicle Exhaust 367

88 Soxhlet Extraction Recoveries of POM from Various Sample Matrices 372

89 Recoveries of POM from Air Particulate and Coal Fly Ash by Ultrasonic Extraction 375

LIST OF FIGURES

Figure		Page
1	Accepted Nomenclature of Benzo(a)pyrene	8
2	Structures of Selected Polycyclic Aromatic Organic Molecules	9
3	Absorption Spectrum of Benzo(a)pyrene in Ethanol	12
4	Hypothesized Ring Closure for a Polycyclic Organic Compound	17
5	POM Formation by Pyrolysis	18
6	Typical Configurations of Conventional Municipal Waste Incinerators	110
7	Typical Configurations of Modular Municipal Waste Incinerators	112
8	Cross Section of a Typical Multiple-hearth Incinerator	126
9	Cross Section of a Fluidized-bed Sewage Sludge Incinerator	127
10	Diagram of a Fluid-bed Catalytic Cracking Process	147
11	Diagram of a Thermofor Catalytic Cracking Process	149
12	Diagram of a Houdriflow Catalytic Cracking Process	150
13	Configuration of a Typical Sintering Facility	159
14	Typical Electric Arc Furnace Ferroalloy Manufacturing Process	166
15	Open Electric Arc Furnace	168
16	Semisealed Electric Arc Furnace	169
17	Sealed Electric Arc Furnace	170
18	Typical Flow Chart for the Production of Low-carbon Ferrochrome by the Exothermic Silicon Reduction Process	172

Figure Page

19 Vacuum Furnace for the Production of Low-carbon Ferrochrome 173

20 Typical Process Flow Diagram for a Sand-cast Iron and Steel Foundry 183

21 General Process Flow Diagram for a By-product Coke Plant 188

22 Typical Asphalt Air Blowing Operation 206

23 Typical Configuration of a Vertical Asphalt Air Blowing Still 208

24 Typical Configuration of a Horizontal Asphalt Air Blowing Still 209

25 Diagram of an Asphalt Roofing Material Manufacturing Line 211

26 Typical Process Used in a Batch-mix Hot Mix Asphalt Plant 229

27 Typical Drum-mix Hot Mix Asphalt Process 231

28 Process Flowsheet for an Oil-furnace Carbon Black Plant 241

29 Sequence of Operations at a Typical Secondary Lead Smelter 254

30 Typical Blast Furnace System for Secondary Lead Production 256

31 Typical Reverberatory Furnace System for Secondary Lead Production 258

32 General Flow Diagram for Primary Aluminum Production 265

33 Aluminum Reduction Cell Diagram 266

34 Flow Diagram for the Production of Prebake Anodes 269

35 Missouri-type Charcoal Kiln 277

36 Multiple-hearth Furnace for Charcoal Production 281

37 Surface Oil Shale Retorting 300

Figure		Page
38	*In Situ* Oil Shale Retorting	302
39	Principal Areas of Oil Shale Deposits in the United States	305
40	Schematic of Modified Method 5 Sampling Train	362
41	Schematic of a SASS Sampling Train	364
42	Diagram of a Vehicle Exhaust Dilution Sampling Arrangement	366
43	Adsorbent Trap for the Collection of Gas-phase POM from Vehicle Exhaust	368
44	Condensation Sampling System for Raw Vehicle Exhaust	370

SECTION 1

PURPOSE OF DOCUMENT

EPA, States and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, limited information is available on the ambient air concentrations of these substances or on the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this that compiles available information on sources and emissions of these substances. This document specifically deals with polycyclic organic matter (POM). Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of POM and making preliminary estimates of the potential for air emissions therefrom.

Because of the limited amounts of data available on POM emissions, and since the configuration of many sources will not be the same as those described herein, this document is best used as a primer to inform air pollution personnel about (1) the type of sources that may emit POM, (2) process variations and release points that may be expected within these sources, and (3) available emissions information indicating the potential for POM to be released into the air from each operation.

The reader is strongly cautioned against using the emissions information contained in this document to try to develop an exact assessment of emissions from any particular facility. Since insufficient data are available to develop statistical estimates of the accuracy of these emission factors, no estimate can be made of the error that could result when these factors are used to calculate emissions for any given facility. It is possible, in some extreme cases, that orders-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment and operating practices. Thus, in situations where an accurate assessment of POM emissions is necessary, source-specific information should be obtained to confirm the existence of particular emitting operations, the types and effectiveness of control measures, and the impact of operating practices. A source test should be considered as the best means to determine air emissions directly from an operation.

SECTION 2

OVERVIEW OF DOCUMENT CONTENTS

As noted in Section 1, the purpose of this document is to assist Federal, State, and local air pollution agencies and others who are interested in locating potential air emitters of POM and making preliminary estimates of air emissions therefrom. Because of the limited background data available, the information summarized in this document does not and should not be assumed to represent the source configuration or emissions associated with any particular facility.

This section provides an overview of the contents of this document. It briefly outlines the nature, extent, and format of the material presented in the remaining sections of this report.

Section 3 of this document provides a brief summary of the physical and chemical characteristics of POM, its basic formation mechanisms, and its potential transformations in ambient air. The fourth section of this document focuses on major sources of POM air emissions. Stationary, mobile, and natural sources of POM air emissions are discussed. For each air emission source category described in Section 4, example process descriptions and flow diagrams are given, potential emission points are identified, and available emission factor information is summarized. The emission factors show the potential for POM emissions from uncontrolled operations as well as operations using controls typically employed in industry. Also presented are the names and locations of all major stationary source facilities identified to be operating and potentially emitting POM. For area sources of POM emissions such as agricultural burning or coal refuse fires, geographic areas where such activities primarily occur are identified.

The fifth section of this document summarizes available procedures for source sampling and analysis of POM. Details are not prescribed nor is any EPA endorsement given to any of these sampling and analysis procedures.

Consequently, this document merely provides an overview of applicable source sampling procedures, citing references for those interested in conducting source tests.

This document does not contain any discussion of health or other environmental effects of POM, nor does it include any discussion of ambient air levels of POM.

Comments on the contents or usefulness of this document are welcomed, as is any information on process descriptions, operating practices, control measures and emissions information that would enable EPA to improve its contents. All comments should be sent to:

Chief, Noncriteria Emissions Section (MD-14)
Air Management Technology Branch
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

SECTION 3
BACKGROUND

NATURE OF POLLUTANT

The term polycyclic organic matter (POM) defines a broad class of compounds which generally includes all organic structures having two or more fused aromatic rings (i.e., rings which share a common border). Polycyclic organic matter has been identified with up to seven fused rings. Theoretically, millions of POM compounds could be formed; however, only about 100 species have been identified and studied.[1]

Eight major categories of compounds have been defined by the U. S. Environmental Protection Agency to constitute the class known as POM.[2,3] The categories are as follows.

1. Polycyclic aromatic hydrocarbons (PAHs) - the PAHs include naphthalene, phenanthrene, anthracene, fluoranthene, acenaphthalene, chrysene, benzo(a)anthracene, cyclopenta(c,d)pyrene, the benzpyrenes, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene, coronene, and some of the alkyl derivatives of these compounds. PAHs are also known as polynuclear aromatics (PNAs).
2. Aza arenes - aza arenes are aromatic hydrocarbons containing a ring nitrogen.
3. Imino arenes - these are aromatic hydrocarbons containing a ring nitrogen with a hydrogen.
4. Carbonyl arenes - these are aromatic hydrocarbons containing one ring carbonyl group.
5. Dicarbonyl arenes - these are also known as quinones, and contain two ring carbonyl groups:
6. Hydroxy carbonyl arenes - these are ring carbonyl arenes containing hydroxy groups and possibly alkoxy or acyloxy groups.

7. Oxa arenes and thia arenes - oxa arenes contain a ring oxygen atom, while thia arenes contain a ring sulfur atom.
8. Polyhalo compounds - some polyhalo compounds, such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), may be considered as POM although they do not have two or more fused aromatic rings.

These categories were developed to better define and standardize the types of compounds considered to be POM.

The two POM chemical groups most commonly found in emission source exhaust and ambient air are PAHs, which contain carbon and hydrogen only, and the PAH-nitrogen analogs. Information available in the literature on POM compounds generally pertains to these PAH groups. Because of the dominance of PAH information (as opposed to other POM categories) in the literature, many reference sources have inaccurately used the terms POM and PAH interchangeably. The majority of information in this section on POM physical/chemical properties, formation mechanisms, and atmospheric persistence pertains to PAH compounds.

Because POM is not one compound but several, it is not possible to describe the nature of all POMs including such information as physical and chemical properties, formation mechanisms, and environmental persistence. Instead, these types of descriptive background information are provided for the primary POM compounds, such as PAHs, that have been identified to exist in air emissions and ambient air. Considerably more voluminous and complex data on POM compound properties and formation theories exist than are presented in this document. The prevalent, more generally applicable information is provided here to build a foundation for understanding the basic nature of POM compounds and POM compound emissions. The literature references cited in this document are excellent sources of specific and greater detail information on POM compounds.

NOMENCLATURE AND STRUCTURE OF SELECTED POMs

In the past, the nomenclature of POM compounds has not been standardized and ambiguities have existed due to different peripheral numbering systems. The currently accepted nomenclature is that adopted by the International Union of Pure and Applied Chemistry (IUPAC) and by the Chemical Abstracts Service.[4] The following rules help determine the orientation from which the numbering is assigned:

1. The maximum number of rings lie in a horizontal row;
2. As many rings as possible are above and to the right of the horizontal row; and
3. If more than one orientation meets these requirements, the one with the minimum number of rings at the lower left is chosen.[5]

The carbons are then numbered in a clockwise fashion, starting with the first counterclockwise carbon which is not part of another ring and is not engaged in a ring fusion. Letters are assigned in alphabetical order to faces of rings, beginning with "a" for the side between carbon atoms 1 and 2 and continuing clockwise around the molecule. Ring faces common to two rings are not lettered. Using these rules, benzo(a)pyrene would have a benzene ring fused to the "a" bond of the parent pyrene structure as shown in Figure 1.

The molecular structures of the more predominantly identified and studied POM compounds (mainly PAHs) are shown in Figure 2.

PHYSICAL PROPERTIES OF POM

Most POM compounds are high melting point/high boiling point solids that appear to be extremely insoluble in water. The PAHs are primarily planar, nonpolar compounds which melt at temperatures well above room temperature. Melting points have been identified for a number of compounds and most values are considerably over $100^{\circ}C$ ($212^{\circ}F$). Phenanthrene, with a

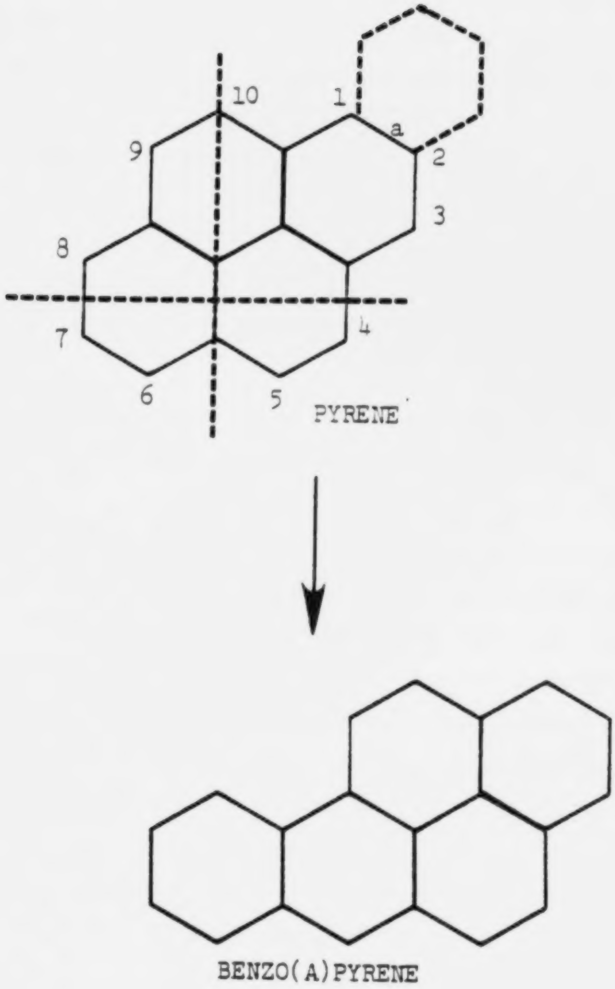

10
1
a
2
9
3
8
7
4
6
5
PYRENE
BENZO(A)PYRENE

Figure 1. Accepted nomenclature for benzo(a)pyrene.[7]

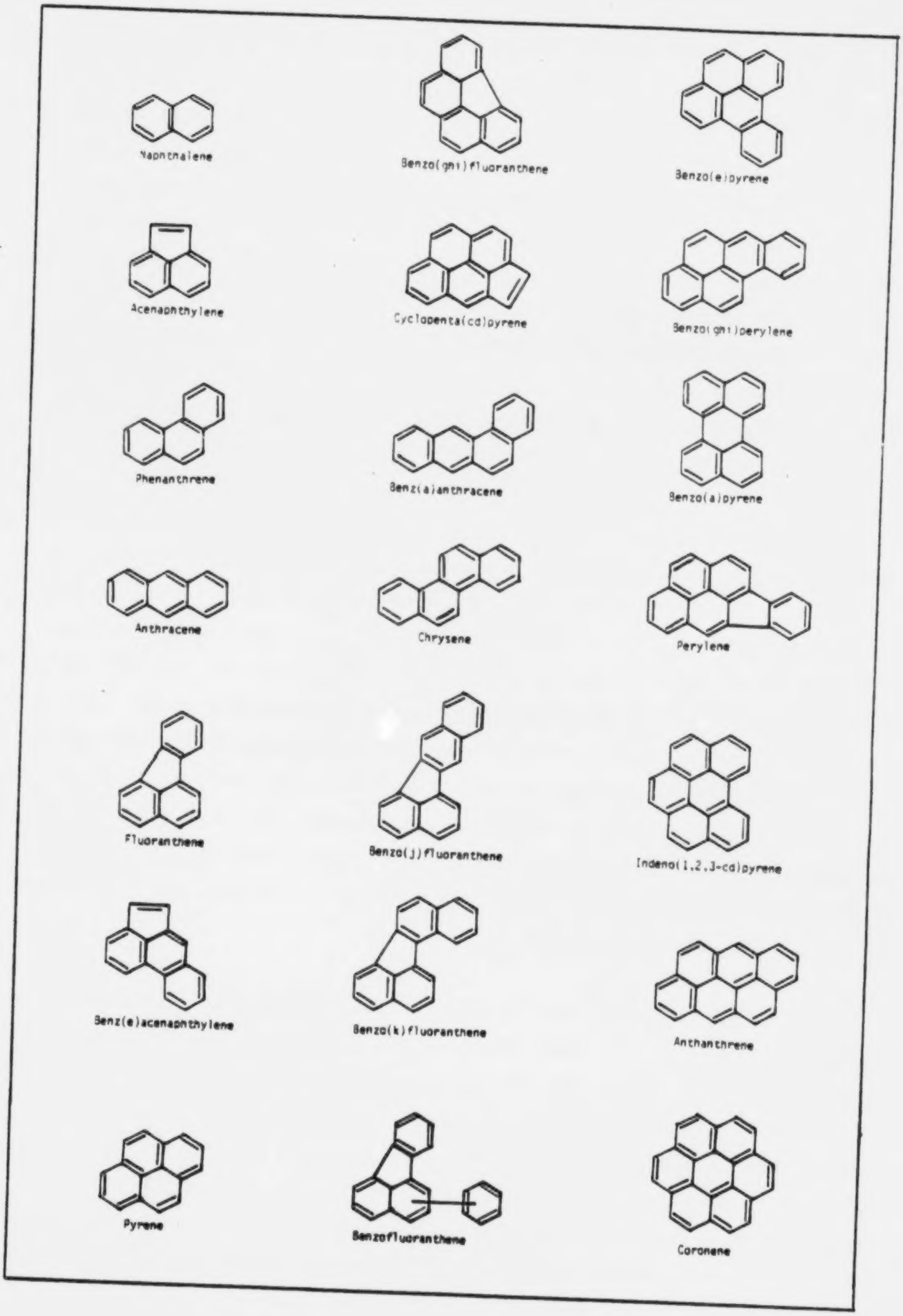

Naphthalene
Benzo(ghi)fluoranthene
Benzo(e)pyrene
Acenaphthylene
Cyclopenta(cd)pyrene
Benzo(ghi)perylene
Phenanthrene
Benz(a)anthracene
Benzo(a)pyrene
Anthracene
Chrysene
Perylene
Fluoranthene
Benzo(j)fluoranthene
Indeno(1,2,3-cd)pyrene
Benz(e)acenaphthylene
Benzo(k)fluoranthene
Anthanthrene
Pyrene
Benzofluoranthene
Coronene

Figure 2. Structures of selected polycyclic aromatic organic molecules.[7]

melting point of 101°C (214°F) and benzo(c)phenanthrene, with a melting point of 68°C (154°F) are two exceptions. An important factor which tends to accompany an increase in melting point is the increase in the number of vertical planes of symmetry. For example, perylene, benzo(a)pyrene, benzo(e)pyrene, and benzo(k)fluoranthrene all have the same molecular weight; however, perylene has the highest melting point and the greatest number of vertical planes of symmetry of the four compounds.[6] Coronene, with six vertical planes of symmetry in addition to its relatively high molecular weight, has a very high melting point of 438°C (820°F). The molecular weights, melting points, and boiling points of selected POM species are listed in Table 1.

The vapor pressures of POM compounds vary depending upon the ring size and the molecular weight of each species. The vapor pressure of pure compounds varies from 6.8×10^{-4} Torr for phenanthrene (3 rings and 14 carbons) to 1.5×10^{-12} Torr for coronene (7 rings and 24 carbons).[7] A POM compound's vapor pressure has considerable impact on the amount of POM that is adsorbed onto particulate matter in the atmosphere and retained on particulate matter during collection of air sampling and during laboratory handling. Retention of POM species on particulates during collection and handling also depends upon temperature, velocity of the air stream during collection, properties of the particulate matter, and the adsorption characteristic of the individual POMs. Table 1 includes vapor pressures at 30°C (86°F) for selected POMs.

The ultraviolet absorption spectra are also available for many POM compounds. Most of the PAHs absorb light strongly at wavelengths longer than 300 nm. The absorption spectra for benzo(a)pyrene, shown in Figure 3, is typical of most of the PAHs.[7] Most of the polycyclic aromatic hydrocarbons absorb light at wavelengths found in sunlight (>300 nm) and are believed to be photochemically reactive by direct excitation. The available spectra data reflect characteristics of PAHs in organic solvents; however, PAHs in the environment are usually particulate-bound and as such may have considerably different absorption properties.

TABLE 1. PHYSICAL PROPERTIES OF VARIOUS POM COMPOUNDS[1,6,7]

Compound	Chemical Formula	Molecular Weight	Melting Point (°C)	Boiling Point[a] (°C)	Vapor Pressure[b] (Torr)
Fluorene	$C_{13}H_{10}$	166.22	116 - 117	295	NR[c]
Carbazole	$C_{12}H_9N$	167.14	246	355	NR
Anthracene	$C_{14}H_{10}$	178.24	216.5 - 217.2	339.9	1.95×10^{-4}
Phenanthrene	$C_{14}H_{10}$	178.24	100 - 101	340	6.8×10^{-4}
Acridine	$C_{13}H_9N$	179.15	111	360	NR
Fluoranthene	$C_{16}H_{10}$	202.26	110.6 - 111.0	393	NR
Pyrene	$C_{16}H_{10}$	202.26	152.2 - 152.9	360	6.85×10^{-7}
Benzo(ghi)fluoranthene	$C_{20}H_{10}$	226.28	147 - 149	NR	NR
Benz(a)anthracene	$C_{18}H_{12}$	228.30	159.5 - 160.5	435	1.1×10^{-7}
Chrysene	$C_{18}H_{12}$	228.30	250 - 254	448	NR
Benzo(a)pyrene	$C_{20}H_{12}$	252.32	176.5 - 177.5	311	5.5×10^{-9}
Benzo(e)pyrene	$C_{20}H_{12}$	252.32	178 - 179	NR	5.54×10^{-9}
Benzo(k)fluoranthene	$C_{20}H_{12}$	252.32	215.5 - 216	NR	9.6×10^{-11}
Perylene	$C_{20}H_{12}$	252.32	273 - 274	500	NR
Benzo(g,h,i)perylene	$C_{22}H_{12}$	276.33	273	NR	1.01×10^{10}
Coronene	$C_{24}H_{12}$	300.36	438	525	1.47×10^{-12}

[a] Each boiling point is at a pressure of 1 atm, except the boiling point of benzo(a)pyrene is at a pressure of 10 torr.

[b] All vapor pressures are at 30°C (86°F).

[c] NR means data not reported.

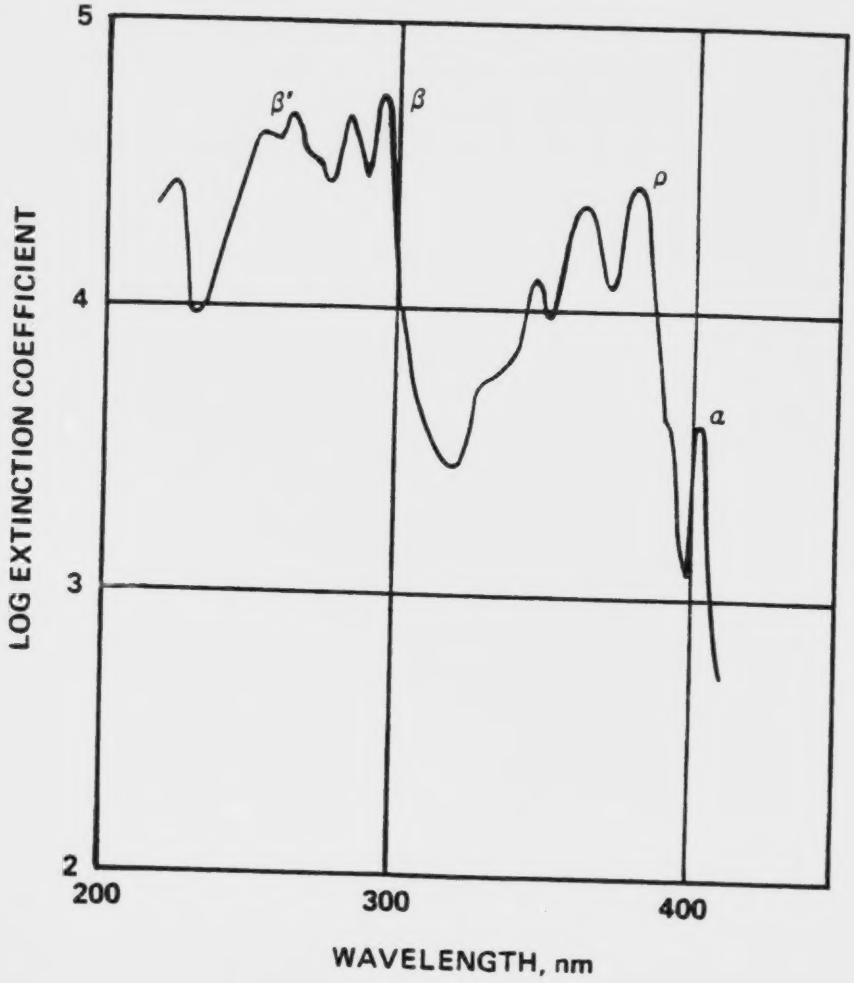


Figure 3. Absorption spectrum of benzo(a)pyrene in ethanol: [, 4030 (3.60); , 3845 (4.44), 3635 (4.36), 3470 (4.10), 3300 (3.76); , 2965 (4.76), 2843 (4.66), 2740 (4.50); 7', 2655 (4.66), 2540 (4.60); ", 2250 (4.44)].

CHEMICAL PROPERTIES OF POM

The chemistry of POMs is quite complex and differs from one compound to another. Most of the information available in the literature concerns the polycyclic aromatic hydrocarbons. Generally, the PAHs are more reactive than benzene and the reactivities toward methyl radicals tend to increase with greater conjugation.[6] Conjugated rings are structures which have double bonds that alternate with single bonds. Conjugated compounds are generally more stable but, toward free radical addition, they are more reactive.[8] For example, in comparison to benzene, naphthalene and benz(a)anthracene, which have greater conjugation, react with methyl radicals 22 and 468 times faster, respectively.

The PAHs undergo electrophilic substitution reactions quite readily. An electrophilic reagent attaches to the ring to form an intermediate carbonium ion; to restore the stable aromatic system, the carbonium ion then gives up a proton. Oxidation and reduction reactions occur to the stage where a substituted benzene ring is formed. Rates of electrophilic, nucleophilic, and free radical substitution reactions are typically greater for the PAHs than for benzene.

Environmental factors also influence the reactivity of PAHs. Temperature, light, oxygen, ozone, other chemical agents, catalysts, and the surface areas of particulates that the PAHs are adsorbed onto may play a key role in the chemical reactivity of PAHs.

POM FORMATION MECHANISMS IN COMBUSTION SOURCES

Polycyclic organic matter formation occurs as a result of combustion of carbonaceous material under reducing conditions. The detailed mechanisms are not well understood; however, it is widely accepted that POM is formed via a free radical mechanism which occurs in the gas phase.[9] As a result, POM originates as a vapor. There is also overwhelming evidence that POM is present in the atmosphere predominantly in particulate form.[10] Therefore, a vapor to particle conversion must take place between the points of formation of POM in the combustion source and its entry to the atmosphere.

It has been recognized that soot (a product of coal combustion) is similar in some structural characteristics to polycyclic aromatic molecules and that both soot and POM are products of combustion.[11] Comparisons of the two types of molecules give rise to the first clue as to how POM may be formed in combustion, namely by incomplete combustion and degradation of large fuel molecules such as coal. It is also known, however, that carbon black and soot are produced by burning methane (CH_4). Thus, it is believed that POMs are not only produced by degrading large fuel molecules, but are also produced by polymerizing small organic fragments in rich gaseous hydrocarbon flames. Before examining POM formation per se, it is instructive to first examine carbon (soot) formation in combustion. The two are similar phenomena and a closer examination of some of the earlier studies on soot formation is helpful in understanding POM formation and behavior.

Soot produced in a flame takes on a number of specific characteristics. Soot or carbon particles may be hard and brittle, soft and fatty, brown to black, and contain anywhere from almost 0 to 50 percent hydrogen (atomically). Generally, it is observed that flame-produced soot is a fluffy, soft material made up of single, almost spherical particles which stick together. Soot properties appear to be independent of the fuel burned in a homogeneous gas flame. However, if hydrocarbon gases (such as methane, propane, or benzene) are passed down a hot tube, the carbon product is quite different from the flame-produced soot. The heterogeneously produced products are hard, long crystals that are shiny and vitreous. The carbon-carbon bonding in these two products is substantially different. The soft, soot product generated from the gas flame possesses carbon-carbon distances of 3.61 to 3.70 Å, while the hard, heterogeneously produced product has a carbon-carbon distance of 3.46 to 3.54 Å.[11,12]

Carbon-producing flames have been identified and labeled as either the acetylenic type or the benzene type. The acetylenic type flame is one in which carbon, as observed in C_2-radiation, is emitted from all parts of the flame. Carbon produced in low molecular weight hydrocarbon flames is made up of benzene and other aromatics (benzene type). Instead of C_2-radiation being emitted from all parts of the flame, a carbon streak is observed that is emitted from the tip of the flame. The basis for the two flame types is related to differences in diffusion properties between the fuel molecule and oxygen. Where the fuel and oxygen are of about the same molecular weight, carbon is observed uniformly in the flame front; where the two differ substantially, enriched pockets of fuel and oxygen occur, and one observes the carbon streak. Thus, the nature of the soot molecule may be independent of the fuel molecule, but its formation is quite dependent on the nature of the fuel and on the method of combustion.[11]

Over the past 20 years, procedures have been developed for analyzing the microstructure and detailed kinetics of processes occurring in flames. A number of investigators have been applying these techniques to studying POM formation in gaseous hydrocarbon flames.[12,13] In one procedure, a pre-mixed hydrocarbon-air flame is stabilized on a burner (usually as a flat flame) and reactants and products are removed with the aid of a microprobe and analyzed by electron microscope or other techniques.[12]

Basically, investigators have been attempting to answer the question: Is POM a precursor to soot formation or is it a by-product of soot formation? It has been observed that the carbon number of the C_xH_y fragment increases and the hydrogen number deceases with distance from the primary flame zone. Most of the C_xH_y fragments contain an even number of carbon atoms. The occurrence of a rapid steady state or equilibrium process has been illustrated by the following steps:

a. $2C_2H_2 \longrightarrow C_4H_2 + H_2$

b. $C_4H_2 + C_2H \longrightarrow C_6H_2 + H$

c. $C_{2n}H_2 + C_2H \longrightarrow C_{2n+2}H_2 + H$

Changes in the molecular weight of POM products as they pass through the flame have been documented. Just above the flame, a large number of POM products are observed, while farther downstream the number of products is considerably reduced.[13] Based on this observation, it appears that a large number of reactive POM products are produced just past the flame zone. These POMs are referred to as reactive POMs, in that they contain many organic side chains (CH_2, C_2H_5, etc.) attached to the rings of the basic POM structures. The reactive POMs, however, degrade in the hot region of the flames so that further downstream only the more stable condensed ring structures are observed.

The changes in POM structure noted above are corroborated in other studies.[12,13] It has been shown that with time a steady increase occurs in the production of lower molecular weight POMs (e.g., anthracene, phenanthrene, fluoranthene, and pyrene), while the higher molecular weight POMs such as benzopyrene, benzoperylene, and coronene reach a maximum and then decline in concentration with increasing distance from the flame. Studies by Toqan et al. show that soot is formed in the region of the flame where a sharp decline of POM compound is observed. They conclude that the POM (particularly PAH) compounds are precursors to soot formation.[13] From the preceding discussion, it is apparent that POM may be a precursor as well as a by-product of soot formation.

The question of how the polyacetylenes (that are produced by a sequence of rapid reaction steps) cyclize still remains. One theory is that the polyacetylene chain bends around the carbon atoms and eventually bonds into the condensed ring structures. Another plausible hypothesis is illustrated in Figure 4. The association shown requires minimum atomic rearrangements. Also, it is highly exothermic, thereby providing sufficient energy to dissociate terminal groups and the free valences to produce reactive and stable POMs.

Pyrolytic studies of aromatic and straight chain hydrocarbons have been conducted which offer logical mechanisms for explaining POM formation.[14] Some examples for explaining the formation of fluoranthene, phenanthrene, and 3,4-benzopyrene are shown in Figure 5. In this instance, the example

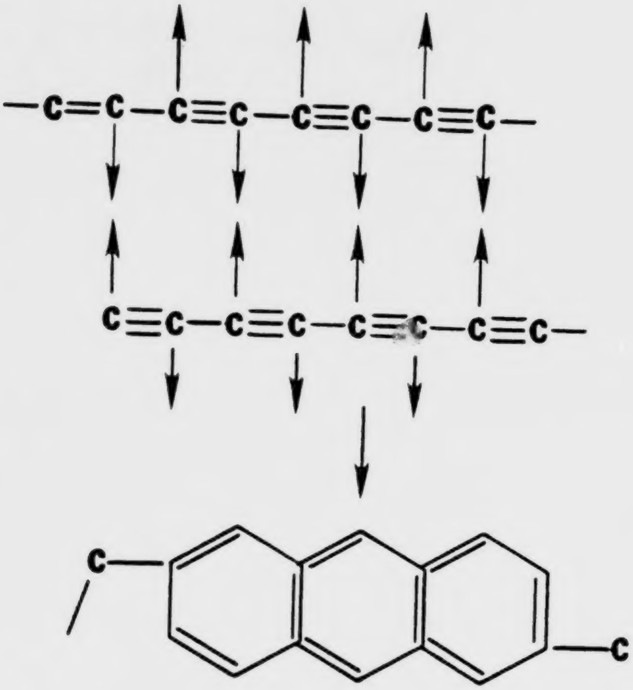


Figure 4. Hypothesized ring closure.[11]

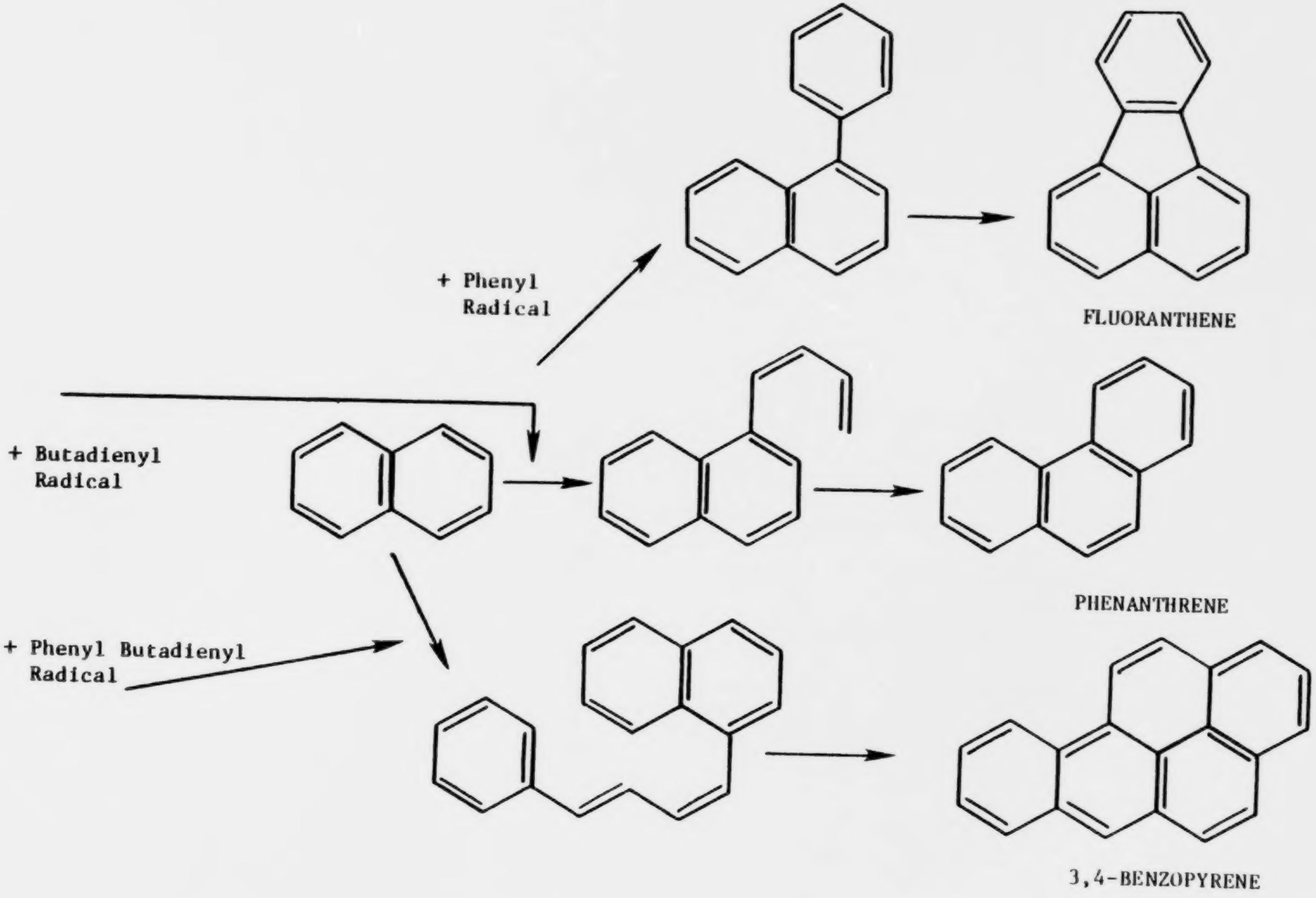

+ Phenyl Radical
FLUORANTHENE
+ Butadienyl Radical
PHENANTHRENE
+ Phenyl Butadienyl Radical
3,4-BENZOPYRENE

Figure 5. POM formation by pyrolysis.[11]

illustrates how phenyl-, butadienyl-, and phenyl butadienyl radicals produced in the pyrolysis of phenylbutadiene may react with naphthalene to produce the three POM products.

In conclusion, there is no single, dominant mechanism for POM formation in flames. In rich gas flames, polyacetylenes can be built up via a C_2H polymerization mechanism. In coal and oil droplet flames, pyrolytic degradation mechanisms prevail. In either instance, soot and POM are related and persist in post-rich flames due to a deficiency of hydroxide radicals.

CONVERSION OF POM FROM VAPOR TO PARTICULATE

Polycyclic organic matter formed during combustion is thought to exist primarily in the vapor phase at the temperatures encountered near the flame. However, POM encountered in the ambient atmosphere is almost exclusively in the form of particulate material.[15] It is thought that the vapor phase material formed initially becomes associated with particles by adsorption as the gas stream cools or possibly by condensation and subsequent nucleation.[15,16] The lack of open-channel porosity, the large concentration of oxygen functional groups on the surface of particulates such as soot, and the adherence of airborne benzo(a)pyrene to the particle in a manner that allows for ready extraction indicate that benzo(a)pyrene and presumably other POM compounds are primarily adsorbed on the surface of particulates through hydrogen bonding.[10]

The physical state of POM in ambient air is determined in part by the amount of particulate generated by the source. Natusch and Tomkins contend that the extent of POM adsorption onto particulate is proportional to the frequency of collision of POM molecules with available surface area, resulting in preferential enrichment of smaller diameter particulates.[17] In areas of high particulate concentrations, such as the stack of a fossil fuel power plant, one would expect nearly complete adsorption of the POM onto particulates. As particulate concentration decreases, as in internal combustion engines, one would expect to find more POM in the condensed phase. In general, the largest concentration of POM per unit of particulate mass will be found in the smaller diameter aerosol particulates. Natusch has developed a detailed mathematical model describing the adsorption and condensation mechanisms of POM compounds.[18] The model can describe the temperature dependence of both adsorption and condensation for several different surface behavioral scenarios.

While both adsorption and condensation may be in operation, it appears that the POM vapor pressures encountered in most combustion sources are not high enough for condensation or nucleation to occur (see Table 1). The saturation vapor pressure or dew point of POM must be attained for these processes to take place. Conversely, adsorption of POM vapor onto the surface of particulate material present in stack or exhaust gases can certainly take place and could account for the occurrence of the particulate POM at ambient atmospheric temperatures. Specifically, the modeling exercises conducted by Natusch have shown that:

1. The most important parameters to be considered in an adsorption model are the adsorption energetics, the surface area, and the vapor phase concentration of the adsorbate.
2. Surface heterogeneity will broaden the temperature range where adsorption becomes significant.
3. The particle surface temperature determines the adsorption characteristics. The gas phase temperature is of secondary importance.
4. For conditions found in a typical coal-fired power plant, homogenous condensation is not highly favored since vapor phase levels of POM are, in most cases, below the saturated vapor concentration.
5. The kinetics of adsorption are predicted to be fast, suggesting that an equilibrium model may be adequate for modeling the adsorption behavior of POM.[19]

Field measurement studies have been conducted to investigate the occurrence of vapor to particle conversion in a combustion source.[18] Measurements were made in the stack system and in the emitted plume of a small coal-fired power plant possessing no particle control equipment. Fly ash samples were collected during the same time periods both inside the stack [temperature at 290°C (554°F)] and from the emitted plume [temperature at 5°C (41°F)]. Collected material was extracted and analyzed for POM. Only crude vapor traps were employed during sample collection so no quantitative measure of vapor phase POM was obtained. It was assumed that all POM collected was in the particulate phase. The results of this field test show that considerably more particulate POM is associated with fly ash collected from the plume at a temperature of 5°C (41°F) than from that collected from the same stream at a temperature of 290°C (554°F). Furthermore, since the two collection points were only 30.5 m (100 ft) apart, quite rapid vapor to particle conversion is indicated.

Laboratory studies have been conducted to determine the rate and extent of POM adsorption onto particulate matter. In one study, a stream of air containing pyrene was passed over a bed of fresh coal fly ash which had previously been shown to contain no detectable POM.[9] The objective was to expose all particles to the same concentration of pyrene for different amounts of time and to determine the specific concentrations of adsorbed pyrene as a function of time at different temperatures. The results of this experiment show that the amount of adsorbed pyrene required to saturate the fly ash increased significantly with decreasing temperature. The rate at which the adsorption process takes place, even at ambient temperatures, is very rapid; on the order of a few seconds. In another study, PAH and soot were sampled from the exhaust gases of a laminar, premixed flat flame under laboratory conditions.[20] Sampling at different filter temperatures was studied to assess partitioning of PAH between vapor phase and soot. The data shown in Table 2 indicate that at low temperatures [40°C (104°F)], the compounds were adsorbed or condensed on the soot particles, while at high temperatures [200°C (392°F)], only the heaviest species were condensed to any significant extent. While these experiments are essentially qualitative, they do establish that coal fly ash and soot will strongly adsorb various POM species, and that the saturation capacity of the adsorbate is inversely related to temperature.

TABLE 2. PERCENT OF TOTAL PAH ASSOCIATED WITH SOOT PARTICLES AS A FUNCTION OF TEMPERATURE[20]

Compound	40°C	55°C	85°C	200°C
Naphthalene	56	6.5	4.3	0.11
Methylnaphthalene	39	a	20	0.00
Biphenyl	89	77	48	0.46
Biphenylene	88	70	66	0.09
Fluorene	98	94	b	2.1
Phenanthrene and Anthracene	90	92	71	4.6
4H-cyclopenta-(d,e,f)phenanthrene	97	b	85	2.3
Fluoranthene	99	b	82	38
Pyrene and Benzacenaphthylene	99	b	83	33

[a] GC/MS analysis not available.

[b] Too much background from contaminants to determine accurate values.

PERSISTENCE AND FATE IN THE ATMOSPHERE

Polycyclic organic matter emitted as primary pollutants present on particulate matter can be subject to further chemical transformation through gas-particle interactions occurring either in exhaust systems, stacks, emission plumes, or during atmospheric transport. When emitted into polluted urban atmospheres, especially photochemical smog with its high oxidizing potential, particle-adsorbed PAH are exposed to a variety of gaseous co-pollutants. These include highly reactive intermediates, both free radicals and excited molecular species and stable molecules. Seasonal variation in transformation reactions of PAH have been observed. During winter, with conditions of low temperature and low irradiation, the major pathway for PAH degradation is probably reactions with nitrogen oxides, sulfur oxides and with the corresponding acids. During summer months, with conditions of high temperatures and intense irradiation, photochemical reactions with oxygen and secondary air pollutants produced by photolysis, such as ozone and hydroxyl and hydroperoxyl radicals, are important.[21]

The PAH group of POM compounds in pure solid or solution form undergo different transformation rates than PAH adsorbed onto other substrates. Because atmospheric PAH is predominately found adsorbed onto particulates, transformation mechanisms discussed in this section concentrate on that form. Numerous studies have shown differences in transformation reactions when various PAHs are present as a pure solid, in solution, or adsorbed onto other solid substrates.[9,16,22,23]

Atmospheric Physics

Because of the high melting and boiling points of materials classified as POM, the bulk of POM is believed to be linked to aerosols in the atmosphere. As POM is mixed with aerosols in the atmosphere, it is spread among particles of widely varied sizes by collision processes. Some information is available on the relationship of POMs to particle size. In one study, DeMaio and Corn found that more than 75 percent of the weight of selected polycyclic hydrocarbons was associated with aerosol particles less than 2.5 um in radius.[24] However, Thomas et al. found that the amount of benzo(a)pyrene per unit weight of soot was constant in the sources tested.[10] A problem in determining the size fractionation of POM-containing aerosols may be due to current sampling methods. Some of the POM may be lost by vaporization from the smaller particles during sample collection. Katz and Pierce observed that the size-mass distribution of PAH-containing particulates varied with collection site. Particulate sampling near vehicular traffic resulted in a group of PAH-particulate compounds in the submicron range, presumably from exhaust, and a second group of large size PAH-particulates (>7.0 um), presumably from roadway reentrainment.[25] Sampling stations located away from highways resulted in over 70 percent of the PAH-particulate mass associated with particles less than or equal to 1.0 um in diameter, which is in agreement with earlier studies.

Particles containing POM are dispersed in air and may be transported great distances from their origin by winds. They are eventually removed from the atmosphere by sedimentation or deposition. Removal is enhanced by washout from under rain clouds and by rainout from within clouds.[26,27] Deposition of large particles by gravitational settling is important, as well as deposition by impaction as air masses flow around obstacles such as rocks, building and vegetation.

Rain clouds play an important role in the removal of POM-laden aerosols from the atmosphere.[27] Aerosols provide centers for nucleation of water droplets in the atmosphere after the air becomes supersaturated with water vapor. Aerosols inside clouds are captured in droplets and rainout occurs. This in-cloud scavenging of particulates is a result of diffusion, interception, and impaction. When precipitation begins to fall from clouds, the droplets sweep out smaller particles and gas-phase POMs during their fall toward the ground. This process, termed washout or below-cloud scavenging, is believed to be significant in removing many pollutants, including POM, from the atmosphere.

The atmospheric half-life (time required for half the material to be removed or destroyed) of POM as a class is estimated to be approximately 100 to 1000 hours under dry conditions for particulate-bound POM.[28] Recent studies of urban aerosols in Pittsburgh, Pennsylvania demonstrated residence times, without precipitation, of from 4 to 40 days for particles less than 1 um in diameter and 0.4 to 4 days for particles 1 to 10 um in diameter.[24] Under precipitation conditions, these times are believed to be somewhat shorter. Studies in Brazil found that under prevailing meteorological and atmospheric conditions, half-life times from 3 days for benzo(a)pyrene to 12.4 days for perylene were typical.[29]

Some of the highly reactive POM compounds are degraded in the atmosphere by reactions with oxidants and by photooxidation.[30] Chemical reactivity of different POM species in the atmosphere may lead to shorter half-lives. Chemical reactivity in the presence of sunlight may lead to transition of POM adsorbed on soot to other material in several hours. A number of different types of POM reactions which occur in the atmosphere and which may affect atmospheric persistence are described in the following sections.

Reactions with Molecular Oxygen

Gas-particle interaction between molecular oxygen and several POM in the absence of irradiation appears to be very slow. Long range transport of POM has been reported in the Nordic countries.[21] In the absence of, or under irradiation with low-intensity light, little evidence for degradation of adsorbed PAH has been shown. However, substantial evidence has been found for photochemical transformation of POM adsorbed on a variety of solids.[26] The photosensitivity of adsorbed PAH is strongly dependent on the nature of the surface on which the compound is adsorbed.[19] A study by Taskar, et al. has shown differences in the reaction of pyrene when adsorbed on carbon, silica and alumina.[22] The half-lives for the degradation of pyrene adsorbed on the three types of particles were similar when in the presence of light. In the dark, however, the half-life of pyrene was approximately twice as long as in light for both silica-bound pyrene, and alumina-bound pyrene, but no difference was observed for carbon-bound pyrene.

A study by Inscoe compared the photo modification of 15 different PAH, deposited on 4 different adsorbents (silica gel, alumina, cellulose, and acetylated cellulose), under exposure to actinic ultraviolet light and room light.[31] Four of the PAHs did not react under any of the test conditions (chrysene, phenanthrene, picene and triphenylene). The other 11 PAH compounds underwent pronounced changes when adsorbed on silica gel and alumina. On the less polar substrates of cellulose and acetylated cellulose, transformations of PAHs were observed but were less extensive and developed more slowly.

Other studies have shown that PAHs adsorbed onto coal fly ash are generally stabilized against photochemical oxidation by comparison with the same compounds present in solution, as the pure solid, or adsorbed onto substrates such as alumina or silica gel.[32,33] This effect has been explained by the hypothesis that the energetic adsorption of PAH onto a highly active surface, such as that of coal fly ash or activated carbon, effectively stabilizes PAH against photooxidation which either increases the electronic excitation energy or decreases the lifetime of the excited state.

Reactions with Ozone

Degradation studies of PAH in solution exposed to ozone may not be relevant to the determination of their half-life on atmospheric particles. Irradiation does not seem to significantly affect the reactivity of PAHs exposed to ozone.[34] Lane and Katz have shown the kinetics of the dark reaction of ozone toward several PAH to be very fast at nearly ambient ozone concentrations.[35] These studies have shown an inverse relationship between the half-life of benzo(a)pyrene and the measured ambient ozone concentrations. Table 3 shows the half-lives of three POM species in simulated daylight subjected to varying concentrations of ozone. It can be seen that as ozone levels increase, the half-lives of each species decrease.

TABLE 3. HALF LIVES IN HOURS OF SELECTED POM IN SIMULATED DAYLIGHT,[a] SUBJECTED TO VARYING CONCENTRATIONS OF ATMOSPHERIC OXIDANTS (OZONE)[35]

Ozone (ppm)	Benzo(k)fluoranthene	Benzo(a)pyrene	Benzo(b)fluoranthene
0.0	14.1	5.3	8.7
0.19	3.9	0.58	4.2
0.70	3.1	0.20	3.6
2.28	0.9	0.08	1.9

[a] Quartzline lamp.

Studies of various PAH compounds adsorbed onto diesel exhaust particulate matter and exposed to ozone have approximated half-lives on the order of 0.5 - 1 hour for most PAH measured.[26] This high reactivity of PAH toward ozone on a natural carbonaceous matrix is probably related to the large specific surface of diesel soot particles as well as to its high adsorptive capacity for several gaseous compounds. Experiments also indicate significant conversion at lower, nearly ambient ozone levels.[21] Eisenberg, et al. have shown that PAH on particulate surfaces are oxidized by low levels of singlet oxygen generated under environmental conditions.[36]

Other Reactions

Two types of free radical processes may be important for particulate organic matter: the gas-particle interactions between hydroxide radicals from the gas phase and particle-associated PAH, or a direct interaction of organic free radicals present at the particle surface. The larger PAHs are extremely sensitive to electrophilic substitution and to oxidation. Nitrogen oxides or dilute nitric acid can either add to, substitute in, or oxidize polycyclic aromatic hydrocarbons. Transformation of some PAH to nitro-PAH has been observed in experiments using relatively low concentrations of nitrogen dioxide and nitric acid.[37,38] The reactions appear to be electrophilic, as electron-donating substituents enhance the reactivity and electron-attracting substituents diminish it. Similar reactions of PAH with atmospheric sulfur dioxide, sulfur trioxide, and sulfuric acid have also been observed.[39]

REFERENCES FOR SECTION 3

1. U. S. Environmental Protection Agency. POM Source and Ambient Concentration Data: Review and Analysis. EPA Report No. 600/7-80-044. U. S. Environmental Protection Agency, Washington, D.C. March 1980.
2. U. S. Environmental Protection Agency. Scientific and Technical Assessment Report on Particulate Polycyclic Organic Matter (PPOM). EPA Report No. 600/6-75-001. U. S. Environmental Protection Agency, Washington, D.C. March 1975.
3. Personal communication between Mr. T. F. Lahre, Air Management Technology Branch, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, and Dr. Larry Johnson, Air and Energy Engineering Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. January 4, 1987.
4. Biologic Effects of Atmospheric Pollutants: Particulate Polycyclic Organic Matter. National Academy of Sciences. Washington, D.C. 1972. pp. 4-12.
5. Loening, Kurt L. and Joy E. Merritt. Some Aids for Naming Polycyclic Aromatic Hydrocarbons and Their Heterocyclic Analogs. In: Polynuclear Aromatic Hydrocarbons: Formation, Metabolism, and Measurement, Proceedings of the Seventh International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1982. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. 1983. pp. 819-843.
6. Tucker, Samuel P. Analyses of Coke Oven Effluents for Polynuclear Aromatic Compounds. In: Analytical Methods for Coal and Coal Products, Volume II, Chapter 43. 1979. p. 163-169.
7. U. S. Environmental Protection Agency. Health Assessment Document for Polycyclic Organic Matter. External Review Draft. EPA Report No. 2/102. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1978. pp. 3-1 to 3-47.
8. Morrison, Robert T. and Robert N. Boyd. Organic Chemistry, Third Edition. Chapter 30, Polynuclear Aromatic Compounds. Allyn and Bacon, Inc. 1978. pp. 967-997.
9. Natusch, D. F. S., W. A. Korfmacher, A. H. Miguel, M. R. Schure, and B. A. Tomkins. Transformation of POM in Power Plant Emissions. In: Symposium Proceedings: Process Measurements for Environmental Assessment, U. S. Environmental Protection Agency, Interagency Energy/Environment R and D Program Report. EPA Report No. 600/7-78-168. Research Triangle Park, North Carolina. 1978. pp. 138-146.
10. Thomas, Jerome, F., Mitsugi Mukai, and Bernard D. Tebbens. Fate of Airborne Benzo(a)pyrene. In: Environmental Science and Technology. 2(1): 33-39. 1968.

11. Polycyclic Organic Materials and the Electric Power Industry. EPRI Report No. EA-787-54. Electric Power Research Institute, Energy Analysis and Environment Division. December 1978. pp. 1-13.

12. Howard, J. B. and J. P. Longwell. Formation Mechanisms of PAH and Soot in Flames. In: Polynuclear Aromatic Hydrocarbons: Formation, Mechanism, and Measurement, Proceedings of the Seventh International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1982. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. 1983. pp. 27-61.

13. Toqan, M., J. M. Beer, J. B. Howard, W. Farmayan, and W. Rovesti. Soot and PAH in Coal Liquid Fuel Furnace Flames. In: Polynuclear Aromatic Hydrocarbons: Formation, Mechanisms, and Measurement, Proceedings of the Seventh International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1982. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. 1983. pp. 1205-1219.

14. Crittenden, B. D. and R. Long. The Mechanisms of Formation Polynuclear Aromatic Compounds in Combustion Systems. In: Carcinogenesis - A Comprehensive Survey, Volume I. Polynuclear Aromatic Hydrocarbons: Chemistry, Metabolism and Carcinogenesis. R. Freudenthal and P. W. Jones, eds. Raven Press, New York, New York. 1976. pp. 209-223.

15. Schure, M. R. and D. F. S. Natusch. The Effect of Temperature on the Association of POM with Airborne Particles. In: Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry, Proceedings of the Sixth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1981. M. Cooke, A. Dennis, and G. Fisher, eds. Battelle Press, Columbus, Ohio. 1982. pp. 713-724.

16. Polycyclic Aromatic Hydrocarbons: Evaluation of Sources and Effects. National Research Council (United States) Committee on Pyrene and Selected Analogues, National Academy of Sciences. National Academy Press, Washington, D.C. 1983. pp. 3-1 to 3-14.

17. Natusch, D. F. S. and B. A. Tomkins. Theoretical Consideration of the Adsorption of Polynuclear Aromatic Hydrocarbon Vapor onto Fly Ash in a Coal-fired Power Plant. In: Carcinogenesis, Volume 3: Polynuclear Aromatic Hydrocarbons: Second International Symposium on Analysis, Chemistry, and Biology. P. Jones and R. Freudenthal, eds. Raven Press, New York, New York. 1978. pp. 145-153.

18. Natusch, David F. S. Formation and Transformation of Polycyclic Organic Matter from Coal Combustion. Prepared under U. S. Department of Energy Contract No. EE-77-S-02-4347. 1978. 34 pp.

19. Natusch, David F. Formation and Transformation of Particulate POM Emitted from Coal-fired Power Plants and Oil Shale Retorting. U. S. Department of Energy. Report No. DOE/EV/04960--TI. U. S. Department of Energy, Washington, D.C. April 1984.

20. Prado, G., P. R. Westmoreland, B. M. Andon, J. A. Leary, K. Biemann, W. G. Thilly, J. P. Longwell, and J. B. Howard. Formation of Polycyclic Aromatic Hydrocarbons in Premixed Flames. Chemical Analysis and Mutagenicity. In: Polynuclear Aromatic Hydrocarbons Chemical Analysis and Biological Fate, Proceedings of the Fifth International Symposium, on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1980. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. 1981. pp. 189-199.

21. Van Cauwenberghe, Karel A. Atmospheric Reactions of PAH. In: Handbook of Polycyclic Aromatic Hydrocarbons: Emission Sources and Recent Progress in Analytical Chemistry. Volume 2: A. Bjorseth and T. Rambahl, eds. Marcel Dekker, Inc. 1985. pp. 351-369.

22. Taskar, P. K., J. J. Solomon, and J. M. Daisey. Rates and Products of Reaction of Pyrene Adsorbed on Carbon, Silica, and Alumina. In: Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods, and Metabolism, Proceedings of the Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1983. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. 1985. pp. 1285-1298.

23. Yokley, Robert A., Arlene A. Carrison, E. L. Wehry, and Gleb Mamantov. Photochemical Transformation of Pyrene and Benzo(a)pyrene Vapor-Deposited on Eight Coal Stack Ashes. Environmental Science and Technology. 20(1): 86-90. 1986.

24. DeMaio, Lawrence and Morton Corn. Polynuclear Aromatic Hydrocarbons Association with Particulates in Pittsburgh Air. In: Journal of Air Pollution Control Association. 16(2): 67-71. 1966.

25. Katz, Morris and Ronald C. Pierce. Quantitative Distribution of Polynuclear Aromatic Hydrocarbons in Relation to Particle Size of Urban Particulates. In: Carcinogenesis, Volume 1. Polynuclear Aromatic Hydrocarbons: Chemistry, Metabolism, and Carcinogenesis. R. Freudenthal and P. Jones, eds. Raven Press, New York, New York. 1976. pp. 412-429.

26. Reference 4, pp. 36-81.

27. Van Noort, Paul C. M. and Erik Wondergem. Scavenging of Airborne Polycyclic Aromatic Hydrocarbons by Rain. Environmental Science and Technology. 19(11): 1044-1049. 1985.

28. Esmen, Nurtan A. and Morton Corn. Residence Time of Particles in Urban Air. Atmospheric Environment. 5(8): 571-578. 1971.

29. Miguel, Antonio H. Atmospheric Reactivity of Polycyclic Aromatic Hydrocarbons Associated with Aged Urban Aerosols. In: Polynuclear Aromatic Hydrocarbons: Formation, Mechanism, and Measurement, Proceedings of the Seventh International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1982. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. 1983. pp. 897-903.

30. Fox, Marge Ann and Susan Olive. Photooxidation of Anthracene on Atmospheric Particulate Matter. Science. 205(10): 582-583. 1979.

31. Inscoe, N. M. Photochemical Changes in Thin Layer Chromatograms of Polycyclic Aromatic Hydrocarbons. Analytical Chemistry. 36: 2505-2506. 1964.

32. Korfmacher, W. A., D. F. S. Natusch, D. R. Taylor, E. L. Wehry, and G. Mamantov. Thermal and Photochemical Decomposition of Particulate PAH. In: Polynuclear Aromatic Hydrocarbons: Chemistry and Biology - Carcinogenesis and Mutagenesis, Proceedings of the Third International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1978. P. Jones and P. Leber, eds. Ann Arbor Science Publishers, Inc. Ann Arbor, Michigan. 1979. pp. 165-170.

33. Korfmacher, W. A., E. L. Wehry, G. Mamantov, and D. F. S. Natusch. Resistance to Photochemical Decomposition of Polycyclic Aromatic Hydrocarbons Vapor-Adsorbed on Coal Fly Ash. Environmental Science and Technology. 14(9): 1094-1099. 1980.

34. Bjorseth, Alf and Bjorn Sortland Olufsen. Long-Range Transport of Polycyclic Aromatic Hydrocarbons. In: Handbook of Polycyclic Aromatic Hydrocarbons. Volume 1. A. Bjorseth, ed. Marcel Dekker, Inc. 1983. pp. 507-521.

35. Lane, Douglas A. and Morris Katz. The Photomodification of Benzo(a)pyrene, Benzo(b)fluoranthene, and Benzo(k)fluoranthene Under Simulated Atmospheric Conditions. In: Fate of Pollutants in the Air and Water Environments. Volume 8, Part 2. J. Pitts and R. Metcalf, eds. Wiley-Interscience, New York. 1977. pp. 137-154.

36. Eisenberg, Walter C., Kevin Taylor, Debra Cunningham, and Robert W. Murray. Atmospheric Fate of Polycyclic Organic Material. In: Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods, and Metabolism, Proceedings of the Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1983. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. 1985. pp. 395-410.

37. Pitts, J. N., Jr., K. A. Van Cauwenberghe, D. Grosjean, J. P. Schmid, D. R. Fitz, W. L. Belser, Jr., G. B. Knudson, and P. M. Hynds. Atmospheric Reactions of Polynuclear Aromatic Hydrocarbons: Facile Formation of Mutagenic Nitro Derivatives. Science. 202: 515-519. 1978.

38. Nielsen, Torben. Reactivity of Polycyclic Aromatic Hydrocarbons Toward Nitrating Species. Environmental Science and Technology. 18(3): 157-163. 1984.

39. Tebbens, Bernard D., Jerome F. Thomas, and Mitsugi Mukai. Fate of Arenes Incorporated with Airborne Soot. American Industrial Hygiene Association Journal. 27(1): 415-421. 1966.

SECTION 4

POM EMISSION SOURCE CATEGORIES

STATIONARY COMBUSTION OF SOLID, LIQUID, AND GASEOUS FUELS FOR HEAT AND POWER GENERATION

Process Description

The combustion of solid, liquid, and gaseous fuels such as coal, lignite, wood, bagasse, fuel oil, and natural gas has been shown through numerous tests to be a source of POM emissions. Polycyclic organic compounds are formed in these sources as products of incomplete combustion. The rates of POM formation and emission are dependent on both fuel characteristics and combustion process characteristics. Emissions of POM can originate from POM compounds contained in fuels that are released during combustion or from high temperature transformations of organic compounds in the combustion zone.[1-3]

Two important fuel characteristics affecting POM formation in combustion sources are (1) the carbon to hydrogen ratio and molecular structure of the fuel and (2) the chlorine and bromine content of the fuel.[1] In general, the higher the carbon to hydrogen ratio, the greater the probability of POM compound formation. Holding other combustion variables constant, the tendency for hydrocarbons present in a fuel to form POM compounds is as follows.

aromatics > cycloolefins > olefins > paraffins

Based on both carbon to hydrogen ratio and molecular structure considerations, the tendency for the combustion of various fuels to form POM compounds is as follows.[1,4]

coal > lignite > wood > waste oil > residual oil > distillate oil

In the formation of chlorinated and brominated POM compounds during stationary source fuel combustion, the chlorine and bromine content of the fuel plays a major role. Based on the chlorine content of fuels, the tendency to form chlorinated POM compounds during combustion is:

bituminous coal > wood > lignite > residual oil > distillate oil

Similarly, based on the bromine content of fuels, the tendency to form brominated POM compounds during combustion is:

bituminous coal > lignite > residual oil > distillate oil > wood

The primary combustion process characteristics affecting POM compound formation and emissions are:[1,5,7]

- combustion zone temperature,
- residence time in the combustion zones,
- turbulence or mixing efficiency between air and fuel,
- air/fuel ratio, and
- fuel feed size.

With adequate residence time and efficient mixing, temperatures in the 800-1000°C (1472-1832°F) range will cause complete destruction of POM compounds such as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs). Concentrations of polyaromatic hydrocarbons (PAHs) also decrease rapidly with increasing temperature.[1]

The most important reason for incomplete combustion of fuel, thereby resulting in POM formation, is insufficient mixing between air, fuel, and combustion products. Mixing is a function of the combustion unit's operating practices and fuel firing configuration. Hand- and stoker-fired solid fuel combustion sources generally exhibit very poor air and fuel mixing relative to other types of combustion sources. Liquid fuel units and pulverized solid fuel units provide good air and fuel mixing.[1,5-7]

The air/fuel ratio present in combustion environments is important in POM formation because certain quantities of air (i.e., oxygen) are needed to stoichiometrically carry out complete combustion. Air supply is particularly important in systems with poor air and fuel mixing. Combustion environments with a poor air supply will generally have lower combustion temperatures and will not be capable of completely oxidizing all fuel present. Systems experiencing frequent start-up and shut-down will also have poor air/fuel ratios. Unburned hydrocarbons, many as POM compounds, can exist in such systems and eventually be emitted through the source stack. Generally, stoker and hand-fired solid fuel combustion sources have problems with insufficient air supply and tend to generate relatively large quantities of POM as a result.[1,6,7]

In solid and liquid fuel combustion sources, fuel feed size can influence combustion rate and efficiency, therefore, POM compound formation is affected. For liquid fuel oils, a poor initial fuel droplet size distribution is conducive to poor combustion conditions and an enhanced probability of POM formation. In most cases, fuel droplet size distribution is primarily influenced by fuel viscosity. As fuel viscosity increases, the efficiency of atomization decreases and the droplet size distribution shifts to the direction of larger diameters. Therefore, distillate oils are more readily atomized than residual oils and result in finer droplet size distribution. This behavior combined with distillate oil's lower carbon to hydrogen ratio means that residual oil sources inherently have a higher probability of POM formation and emission then distillate oil sources.[1,5,6]

For solid fuels, fuel size affects POM formation by significantly impacting combustion rate. Solid fuel combustion involves a series of repeated steps, each with the potential to form POM compounds. First, the volatile components near the surface of a fuel particle are burned followed by burning of the residual solid structure. As fresh, unreacted solid material is exposed, the process is repeated. Thus, the larger the fuel particle, the greater the number of times this sequence is repeated and the longer the residence time required to complete the combustion process. With succeeding repetitions, the greater the probability of incomplete combustion and POM formation. Again, stoker and hand-fired solid fuel combustion units represent the greatest potential for POM emissions due to fuel size considerations.[1]

Polycyclic organic matter can be emitted from fuel combustion sources in both gaseous and particulate phases. The compounds are initially formed as gases, but as the flue gas stream cools, a portion of the POM constituents adsorb to solid fly ash particles present in the stream. The rate of adsorption is dependent on temperature, and on fly ash and POM compound characteristics. At temperatures above 150°C (302°F), most POM compounds are expected to exist primarily in gaseous form. In several types of fuel combustion systems, it has been shown that POM compounds are preferentially adsorbed to smaller (submicron) fly ash particles because of their larger surface area to mass ratios. These behavioral characteristics of POM emissions are important in designing and assessing POM emission control systems.[1,6,8,9]

The primary stationary combustion sources emitting POM compounds are boilers, furnaces, heaters, stoves, and fireplaces used to generate heat and/or power in the utility, industrial, commercial, and residential use sectors. A description of the combustion sources and their typical emission control equipment within each of these major use sectors is given below.

Utility Sector--

The utility combustion sector consists of units burning predominantly coal, oil, and natural gas to generate steam for electricity production. Coal combustion at utilities is accomplished by using pulverized coal (dry or wet bottom) boilers, cyclone boilers, or spreader stoker boilers. Pulverized dry bottom coal boilers currently dominate the utility sector and are expected to increase in dominance in the future. Pulverized wet bottom and cyclone coal boilers are no longer sold due to their inability to meet nitrogen oxides (NO_x) emission standards. Stoker coal boilers, currently accounting for less than 1 percent of the utility sector total, are obsolete due to their inefficiency and are now being retired. Variation in the types of oil- and gas-fired units used in the utility sector is not as great as for coal units. Most oil-fired and gas-fired boilers utilize a tangential firing design.[4,6]

Utility boilers are generally the best controlled of all fuel combustion sources. Existing emission regulations for total particulate matter (PM) and sulfur dioxide (SO_2) have necessitated controls on coal- and oil-fired utility sources. Emission controls are not required on natural gas boilers because uncontrolled emissions are inherently low relative to coal and oil units.[6] Baghouses, ESPs, wet scrubbers, and multicyclones have been applied for PM control in the utility sector. Particulate POM, particularly fine particles, would be controlled most effectively by baghouses or ESPs. No control of gaseous POMs would be achieved by baghouse and ESP systems. Wet scrubbers could potentially be effective for controlling particulate and gaseous POM. Scrubbers would condense the POM compounds existing as vapors and collect them as the gas stream is saturated in the scrubber. Multicyclones would be the poorest control system for POM emissions because they are ineffective on fine particles and would have no control effect on gaseous POM.[4,6]

The most common SO_2 control technology currently used on utility boilers is lime/limestone flue gas desulfurization (FGD). This technology employs a wet scrubber for SO_2 removal and is often preceded by an ESP, which accomplishes the bulk of PM control. Wet FGD/ESP systems, while providing for the control of POM condensed on particulate matter at the entrance to the ESP, have been shown to poorly control vapor phase POM. Tests examining benzo(a)pyrene showed that condensation of the vapor phase POM compound would occur in the scrubber, but significant collection of POM particles remaining in the gas flow through the scrubber was not achieved.[4,6]

A more recently applied SO_2 control technique for utility boilers is spray drying. In this process, the gas stream is cooled in the spray dryer but remains above the saturation temperature. A fabric filter or an ESP is located downstream of the spray dryer, thus providing for significant control of both particulate and vapor phase POM because the vapor phase compounds are condensed before they reach the baghouse or ESP.[4,6]

Nitrogen oxide control techniques for utility boilers such as low excess air firing and staged combustion may act to increase POM compound formation. The principle of these NO_x control techniques is to limit the oxygen available for NO_x formation in the combustion zone. Limiting oxygen effects a lower air/fuel ratio and may cause increased POM formation. Data to completely characterize the effect of combustion source NO_x controls on POM emissions are very limited and inconsistent.[4,6]

Industrial Sector--

Boilers are used in industry primarily to generate process steam and to provide for space heating. The most common type of coal-fired industrial unit is a pulverized coal boiler; however, stoker units (mainly spreader stokers) are also prevalent. A need for large coal-fired boilers is usually serviced with pulverized coal units. Smaller needs are typically met with underfeed and overfeed stokers. Spreader stokers are found across the entire industrial boiler size range.[4,6]

For sources burning oil or natural gas, the most common combustion designs are watertube and firetube boilers. Wood-fired and bagasse-fired industrial boilers are predominantly stoker designs. Wood boilers are often equipped with multicyclones to capture large, partially burned material and reinject it to the boiler.[4,6]

Emission controls for coal-fired industrial boilers and their effect on POM emissions are very similar to those previously described for coal-fired utility boilers. Particulate matter control in the industrial sector is being achieved by the use of baghouses, ESPs, wet scrubbers, and multicyclones. For SO_2 control, FGD systems are much less frequent in the industrial sector as opposed to the utility sector; however, they are used. Generally, in the industrial sector, SO_2 regulations are met through the burning of lower sulfur content compliance coals.[4,6]

Particulate matter emissions from oil-fired industrial boilers are generally not controlled under existing regulations because emission rates are low relative to coal-fired sources. Some areas may limit SO_2 emissions from oil firing by specifying the use of lower sulfur content oils. Natural gas industrial boilers are not subject to current PM or SO_2 emission standards because of very low emissions relative to coal and oil sources.[4,6]

Wood-fired industrial boilers are typically controlled by multicyclones followed by venturi or impingement-type wet scrubbers. A limited number of wood-fired boiler installations have also used ESPs for control. The effect of both of these control systems on POM emissions reduction is estimated to be similar to that obtained at coal-fired units using the same technology (i.e., potentially good particulate and vaporous POM control with scrubbers and effective particulate POM, but no vaporous POM control with ESPs). Bagasse-fired boilers are also controlled with predominantly wet scrubbers and, to a lesser extent, multicyclones.[4,6]

Commercial/Institutional Sector--

The commercial/institutional category includes such facilities as hospitals, schools, office buildings, and apartment buildings. Boilers and furnaces at commercial/institutional facilities are used primarily to provide space heat. Oil- and natural gas-fired units predominate over coal in this category. These units are generally of a firetube or cast iron design. Coal-fired boilers are primarily underfeed stokers, with some pulverized coal and spreader stoker units in use at large facilities.[4,6]

Unless the facilities are unusually large, emissions control at commercial/institutional sources is marginal or even nonexistent. In boilers with controls, the control system generally only consists of multicyclones. Multicyclones would effect some control on larger particulate POM, but would have no control impact on fine particulate POM and gaseous POM compounds.[4,6]

Residential Sector--

The residential sector includes furnaces burning coal, oil, and natural gas and stoves and fireplaces burning coal and wood to produce heat for individual homes. Residential coal-fired furnaces are usually underfeed or hand-stoked units. Oil- and gas-fired residential furnaces are designed with varying burner configurations, each attempting to optimize fuel combustion efficiency. In oil-fired units, pressure or vaporization is used to atomize fuel oil in an effort to produce finer droplets for combustion. Finer droplets generally mean more complete combustion and less POM formation. In gas-fired units, excess air is often premixed with the natural gas fuel prior to injection in the burner to increase combustion efficiency. Wood-fired stoves have varying designs based on the use or non-use of baffles and catalysts, the extent of combustion chamber sealing, and differences in air intake and exhaust systems. Wood stove design and operation practices are important determinants of POM formation in wood-fired sources.[4,6]

Residential combustion sources are generally not equipped with particulate matter or gaseous pollutant control devices. In coal- and wood-fired sources, stove design and operating practice changes have been made to effect lower particulate matter, hydrocarbon, and carbon monoxide emissions. Changes include modified combustion air flow control, better thermal control and heat storage, and the use of combustion catalysts. Such changes can conceivably lead to reduced POM formation and emission.[4,6]

Emission Factors

Emissions data for stationary fuel combustion sources constitutes the bulk of the POM emissions data available in the literature. Because of their propensity to form and release POM emissions, fuel combustion sources have been air emission tested in much greater numbers than any other POM emission source category. In the evaluation and comparison of POM emission factors for the fuel combustion source category, consideration should be given to:

- the methods used to take and analyze samples,
- the measurement of particulate POM only or of gaseous and particulate POM,
- the physical phase in which emissions predominantly occur,
- the number of POM compounds analyzed for, and
- the specific POM compounds analyzed for.

The literature contains POM emission factor data that span from the early 1960s to the present. Methods used in past source tests to sample for and analyze POM compounds from combustion sources have varied considerably with respect to sample collection, preservation, preparation, and component analysis techniques. Because of this variability, it is often difficult to make valid comparisons of POM emission results because the forms, species, and sensitivity of measurements may be grossly different between tests even though both report a total POM result.

One important factor affecting the comparability of results involves whether the sample collection technique attempted to collect gaseous as well as particulate POM. Many of the earlier source tests used only a standard EPA Method 5 sample collection procedure and thus did a less than adequate job of collecting many POM compounds emitted in gaseous form. More recently, a Modified Method 5 approach has become popular for combustion source testing. The Modified Method 5 approach employs a resin filter to trap condensible organics including POM. Because gaseous POM have been shown to often be dominant in total combustion source POM emissions, the inclusion of a gaseous POM collection procedure is important. Knowing the physical forms of POM sampled for in a test is crucial to being able to compare one test's results with those of another test of the same or similar source.

In the evaluation and comparison of any total POM emissions data, some definition must be known or established as to what constitutes total POM. As discussed in Section 3, the number of POM compounds that conceivably may be formed during combustion processes runs into the hundreds. Few, if any, source tests analyze for that many compounds. The majority of the combustion source POM emission tests in the literature analyzed for less than 25 specific POM compounds. The largest number of compounds analyzed for was 56. Thus, when one test analyzed for only 10 POM compounds and one other for 25 POM compounds, total POM results will not be comparable between the two tests.

In assessing the number of specific POM compounds analyzed, the specific compounds analyzed for should also be carefully evaluated. In many combustion source tests for POM emissions, the 25 POM compounds expected to occur in the largest quantity are analyzed for. Other tests, however, analyze for POM compounds on the basis of compound toxicity such that several compounds that may occur in only minute proportions, but are highly toxic, are analyzed for at the expense of high volume/low toxicity compounds.

The exclusion or inclusion of specific compounds can be highly important in the evaluation and comparison of POM emissions data. Naphthalene generally constituted a sizable portion of total POM emissions in the tests where it was measured. However, it is viewed as having a low toxicity relative to other POM compounds [e.g., benzo(a)pyrene]. Other tests, more concerned with the quantification of toxic POM emissions from combustion sources, did not include naphthalene in the list of analyzed compounds and, therefore, had a significantly lower total POM value than those that did.

The technical literature contains emission factor data for POM for the following categories of fuel combustion.

- utility coal combustion
- industrial coal combustion
- commercial and residential coal combustion
- residual oil combustion
- distillate oil combustion
- industrial and commercial wood combustion
- residential wood combustion
- natural gas combustion
- bagasse combustion
- waste oil combustion

The factors for each category are presented in Tables 4 to 18 and are described below.

Utility Coal Combustion--

Emissions data on POM from coal-fired utility boilers are presented in Table 4 (pulverized coal units), Table 5 (cyclone units), and Table 6 (stoker units). For pulverized coal boilers controlled with ESPs, total POM emissions (particulate and gaseous) have been reported to range from 0.30 to 8.0 pg/J (0.7 to 18.6 $lb/10^{12}$ Btu). Naphthalene and phenanthrene accounted for the majority of total POM emissions.[5,7,10-12]

Pulverized coal boilers controlled by a multicyclone/ESP combination exhibited a total particulate POM emissions range of 0.30 to 0.95 pg/J (0.7 to 2.2 $lb/10^{12}$ Btu). Predominant POM compounds in these emissions were pyrene, fluoranthene, benzo(a)pyrene, and benzo(g,h,i)perylene. Total particulate and gaseous POM emissions from multicyclone/ESP-controlled pulverized coal boilers ranged from 0.014 to 8.0 pg/J (0.033 to 18.6 $lb/10^{12}$ Btu). Naphthalene and biphenyl constituted the bulk of total particulate and gaseous POM emissions.[5,7,10-12]

TABLE 4. POM EMISSION FACTORS FOR PULVERIZED COAL UTILITY BOILERS

Boiler Characteristics	Coal Type	Controls Used	Total POM Emission Factor pg/J-Heat Input (lb/10^{12} Btu-Heat Input)	Reference
Horizontally Opposed	a	a	0.013 - 1.95 (0.03 - 4.5)^{b,c}	7
Front Wall-Fired	a	a	0.57 (1.1)^{b,d}	7
Corner Fired	a	a	0.93 - 1.2 (2.2 - 2.7)^{b,e}	7
Vertically-Fired	a	a	0.14 - 0.68 (0.32 - 1.6)^{b,f}	7
Dry Bottom	a	a	0.34 (0.8)^{g}	5
Tangentially-Fired	Subbituminous	ESP	0.30 (0.7)^{h}	10
Vertically-Fired	Bituminous	ESP	2.80 (6.5)^{h}	10
Front Wall-Fired	Bituminous	ESP	0.73 (1.7)^{i}	10
Dry Bottom	Bituminous	Wet Scrubber	3.68 (8.55)^{j,k}	11
Dry Bottom	Bituminous	Multicyclone/ESP	0.014 (0.033)^{j,l}	11
Dry Bottom	Bituminous	Multicyclone/ESP	8.0 (18.6)^{j,m}	11
Wet Bottom	Bituminous	ESP	8.0 (18.6)^{j,n}	11
Wet Bottom	Bituminous	Wet Scrubber	243.1 (565)^{j,o}	11
Dry Bottom, Front Wall-Fired	Lignite	Multicyclones	7.9 (18.3)^{j,p}	11
Dry Bottom, Front Wall-Fired	Lignite	Multicyclones	0.78 (1.8)^{j,p}	11
Dry Bottom, Front Wall-Fired	Lignite	ESP	1.1 (2.6)^{j,p}	11
Dry Bottom, Vertically-Fired	a	None	0.32 - 4.2 (0.75 - 9.7)^{q,r}	12
Dry Bottom, Vertically-Fired	a	Multicyclone/ESP	0.30 - 0.70 (0.7 - 1.6)^{q,s}	12
Dry Bottom, Front Wall-Fired	a	ESP	0.17 - 0.60 (0.4 - 1.4)^{q,t}	12
Dry Bottom, Tangentially-Fired	a	Multicyclone/ESP	0.95 (2.2)^{q,u}	12
Wet Bottom, Opposed-Fired	a	Multicyclones	0.34 - 2.0 (0.8 - 4.6)^{q,v}	12

---

[a] Data not reported in available literature.

[b] Factor represents only particulate POM emissions.

TABLE 4. POM EMISSION FACTORS FOR PULVERIZED COAL UTILITY BOILERS (Continued)

---

[c] Specific POM compounds identified in these emissions include benzo(a)pyrene, benzo(g,h,i)perylene, coronene, 7,12-dimethyl benz(a)anthracene, fluoranthene, 3-methylcholanthrene, benzo(e)pyrene, and pyrene.

[d] The primary constituents of total POM emissions were benzo(e)pyrene (45 percent), pyrene (35 percent), fluoranthene (16 percent), benzo(a)pyrene (4 percent), and benzo(g,h,i)perylene (1 percent).

[e] Specific POM compounds identified in these emissions include anthanthrene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(g,h,i)perylene, coronene, fluoranthene, perylene, phenanthrene, and pyrene. The primary constituents of total POM emissions were fluoranthene (33-40 percent), benzo(g,h,i)perylene (12-15 percent), pyrene (12-14 percent), and benzo(a)pyrene (12-14 percent).

[f] Specific POM compounds identified in these emissions include benz(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(g,h,i)perylene, fluoranthene, perylene, phenanthrene, and pyrene. The principal constituents of total POM emissions were fluoranthene (36-53 percent), pyrene (22-42 percent), and benzo(a)pyrene (3-17 percent).

[g] Factor represents predominantly particulate POM. Eleven specific POM compounds were analyzed for during these tests. Specific compounds identified were pyrene, benzo(a)pyrene, benzo(e)pyrene, fluoranthene, and benz(a)anthracene. Pyrene and fluoranthene accounted for 90 percent of total POM emissions.

[h] Factor represents both particulate and gaseous POM. Nine specific POM compounds were analyzed for during these tests. Specific compounds identified were naphthalene, acenaphthylene, fluorene, phenanthrene, fluoranthene, pyrene, chrysene, and benzo(a)pyrene. Naphthalene and phenanthrene accounted for 85 percent of total POM emissions.

[i] Factor represents both particulate and gaseous POM. Nine specific POM compounds were analyzed for during these tests. Specific compounds identified were naphthalene, fluorene, phenanthrene, fluoranthene, and chrysene. Naphthalene and phenanthrene accounted for about 91 percent of total POM emissions.

[j] Factor represents both particulate and gaseous POM. Fifty-six specific POM compounds were analyzed for during these tests.

[k] Specific compounds identified were biphenyl, benzo(g,h,i)perylene, o-phenylenepyrene, dibenz(a,h)anthracene, picene, and dibenz(a,c)anthracene. Benzo(g,h,i)perylene, o-phenylenepyrene, and dibenz(a,h)anthracene accounted for about 82 percent of total POM emissions.

[l] Specific compounds identified were phenyl naphthalene and biphenyl, with phenyl naphthalene constituting 66 percent of total POM emissions.

[m] Specific compounds identified were naphthalene and biphenyl, with naphthalene constituting 90 percent of total POM emissions.

[n] Specific compounds identified were naphthalene and phenanthrene, with naphthalene constituting 73 percent of total POM emissions.

[o] Specific compounds identified were naphthalene, biphenyl, phenanthrene, pyrene, fluoranthene, chrysene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-c,d)pyrene. Total POM emissions consisted primarily of naphthalene (26 percent), phenanthrene (23 percent), pyrene (16 percent), and chrysene (10 percent).

[p] Reported value is for trimethyl propenyl naphthalene.

[q] Factor represents predominantly particulate POM. Ten specific POM compounds were analyzed for during these tests.

[r] Specific compounds identified were benzo(a)pyrene, pyrene, benzo(g,h,i)perylene, anthanthrene, fluoranthene, benzo(e)pyrene, perylene, coronene, anthracene, and phenanthrene. Fluorene, phenanthrene, and pyrene were generally the predominant POM compounds measured.

[s] Specific compounds identified were benzo(a)pyrene, pyrene, fluoranthene, benzo(e)pyrene, perylene, and benzo(g,h,i)perylene. Pyrene and fluoranthene were generally the dominant POM compounds measured. However, in one test, total POM emissions consisted of the following distribution: benzo(a)pyrene (27 percent), fluoranthene (18 percent), benzo(e)pyrene (17 percent), benzo(g,h,i)perylene (18 percent), and pyrene (16 percent).

[t] Specific compounds identified were benzo(a)pyrene, pyrene, benzo(e)pyrene, benzo(g,h,i)perylene, phenanthrene, and fluoranthene. Pyrene, phenanthrene, and fluoranthene accounted for the majority of total POM emissions.

[u] Specific compounds identified were benzo(a)pyrene, pyrene, benzo(e)pyrene, perylene, benzo(g,h,i)perylene, anthanthrene, coronene, phenanthrene, and fluoranthrene. Fluoranthene, pyrene, benzo(a)pyrene, and benzo(g,h,i)perylene accounted for 80 percent of total POM emissions.

[v] Specific compounds identified were benzo(a)pyrene, pyrene, fluoranthene, coronene, benzo(g,h,i)perylene, and benzo(e)pyrene. Benzo(g,h,i)-perylene, fluoranthene, and benzo(e)pyrene were the compounds generally constituting the majority of total POM emissions.

TABLE 5. POM EMISSION FACTORS FOR COAL-FIRED, CYCLONE UTILITY BOILERS

Coal Type	Controls Used	Total POM Emission Factor pg/J-heat input ($lb/10^{12}$ Btu-heat input)	Reference
[a]	ESP	0.5 - 3.2 (1.2 - 7.4)[b]	12
[a]	[a]	1.8 (4.3)[c]	7
Bituminous	ESP	0.88 (2.04)[d]	10
Bituminous	ESP	0.20 (0.46)[d]	10
Bituminous	ESP	24.6 (57.2)[e,f]	11
Bituminous	ESP	1.2 (2.7)[e,g]	11
Lignite	ESP	0.05 (0.11)[e,h]	11
Lignite	ESP	0.68 (1.6)[e,i]	11
Bituminous	ESP	2.4 (5.6)[e,j]	11
Bituminous	Wet Scrubber	7.0 (16.2)[e,k]	11

[a] Data were not reported in the available literature.

[b] Factor represents predominantly particulate POM emissions. Ten specific POM compounds were analyzed for during these tests. Specific compounds identified were benzo(a)pyrene, pyrene, benzo(e)pyrene, perylene, benzo(g,h,i)perylene, coronene, and fluoranthene. Pyrene, benzo(e)pyrene, benzo(a)pyrene, and benzo(g,h,i)perylene accounted for the majority of total POM emissions.

[c] Factor represents only particulate POM emissions. The principal constituents of total POM emissions were pyrene (53 percent), benzo(e)pyrene (20 percent), benzo(a)pyrene (11 percent), benzo(g,h,i)perylene (10 percent), and fluoranthene (4 percent).

[d] Factor represents both particulate and gaseous POM emissions. Nine specific POM compounds were analyzed for during these tests. Specific compounds identified were naphthalene, fluorene, phenanthrene, and chrysene. Naphthalene constituted from 90 to 99 percent of total POM emissions.

[e] Factor represents both particulate and gaseous POM emissions. Fifty-six specific POM compounds were analyzed for during these tests.

[f] Reported value is for naphthalene. No other POM compounds were detected.

TABLE 5. POM EMISSION FACTORS FOR COAL-FIRED, CYCLONE UTILITY BOILERS (Continued)

---

[g] Reported value is for phenyl naphthalene. No other POM compounds were detected.

[h] Reported value is for biphenyl. No other POM compounds were detected.

[i] Reported value is for trimethyl propenyl naphthalene. No other POM compounds were detected.

[j] Specific compounds identified were ethyl biphenyl, phenanthrene, and methylphenthrene. Methylphenthrene constituted 84 percent of total POM emissions.

[k] Specific compounds identified were biphenyl, decahydronaphthalene, ditert-butyl naphthalene, dimethyl isopropyl naphthalene, hexamethyl biphenyl, hexamethyl hexahydro indacene, dihydronaphthalene, C_{10} substituted naphthalene, C_{10} substituted decahydronaphthalene, methyl naphthalene, anthracene/phenanthrene, 9,10-dihydronaphthalene/1-1' diphenylethene, 1,1'-bis (p-ethylphenyl)-ethane/tetramethyl biphenyl, 5-methyl-benz-c-acridine, and 2,3-dimethyl decahydronaphthalene. Biphenyl, 1,1-bis(p-ethylphenyl)-ethane/tetramethyl biphenyl, and methyl naphthalene constitute almost 80 percent of total POM emissions.

TABLE 6. POM EMISSION FACTORS FOR COAL-FIRED, STOKER UTILITY BOILERS

Boiler Characteristics	Coal Type	Controls Used	Total POM Emission Factor pg/J-heat Input ($lb/10^{12}$ Btu-heat Input)	Reference
Spreader, Traveling Grate	a	Multicyclones	<0.054 - 0.20 (0.13 - 0.47)[b]	12
Chain Grate	a	a	49.1 (114)[c]	7
Spreader	a	a	0.20 (0.46)[d]	7
Chain Grate	a	a	1.2 (2.7)[e]	5
a	Bituminous	Baghouse	39.6 (92.1)[f,g]	11
a	Bituminous	Multicyclones	5.2 (12.0)[f,h]	11
Spreader	Lignite	Multicyclones	6.3 (14.6)[f,i]	11

[a] Data not reported in the available literature.

[b] Factor represents primarily particulate POM emissions. Ten specific POM compounds were analyzed for during these tests. Specific compounds identified were benzo(a)pyrene, pyrene, benzo(e)pyrene, coronene, and fluoranthene. Pyrene, fluoranthene, and benzo(e)pyrene constitute the majority of total POM emissions.

[c] Factor represents only particulate POM emissions. The primary constituents of total POM emissions were fluoranthene (30 percent), pyrene (22 percent), phenanthrene (22 percent), benzo(a)pyrene (15 percent), benzophenanthrene (5 percent), and 1,2-benzofluorene (4 percent).

[d] Factor represents only particulate POM emissions. The primary constituents of total POM emissions were pyrene (50 percent), fluoranthene (24 percent), benzo(e)pyrene (14 percent), benzo(a)pyrene (<10 percent), and coronene (3 percent).

[e] Factor represents primarily particulate POM emissions. Eleven specific POM compounds were analyzed for during these tests. Specific compounds identified were benzo(a)pyrene, pyrene, benzo(e)pyrene, and fluoranthene. Fluoranthene and pyrene accounted for about 87 percent of total POM emissions.

[f] Factor represents both particulate and gaseous POM emissions. Fifty-six specific POM compounds were analyzed for during these tests.

[g] Specific compounds identified were naphthalene and a mixture of 3,8-dimethyl-5-(1-methyl ethyl)-1,2-naphthalene dione and trimethyl naphthalene. The naphthalene mixture constituted 97 percent of total POM emissions.

[h] Specific compounds identified were naphthalene, phenyl naphthalene, and 2-ethyl-1,1'-biphenyl. Phenyl naphthalene and 2-ethyl-1,1'-bipheny constituted 96 percent of total POM emissions.

[i] Reported value is for trimethyl propenyl naphthalene. No other POM compounds were detected.

Total particulate POM emissions from multicyclone-controlled pulverized coal boilers were found to range from 0.34 to 2.0 pg/J (0.8 to 4.6 lb/10^{12} Btu). Benzo(g,h,i)perylene, fluoranthene, and benzo(e)pyrene generally constituted the bulk of total particulate POM from this source. Total particulate and gaseous POM emissions from pulverized coal units controlled by multicyclones ranged from 0.78 to 7.9 pg/J (1.8 to 18.3 lb/10^{12} Btu), with trimethyl propenyl naphthalene constituting 100 percent of the emissions.[5,7,10-12]

Pulverized coal boilers controlled by wet scrubbers had the largest variability in total POM emissions of the controlled pulverized coal utility boilers. Total particulate and gaseous POM emissions ranged from 3.68 to 243.1 pg/J (8.55 to 565 lb/10^{12} Btu), with naphthalene, phenanthrene, benzo(g,h,i)perylene, and o-phenylenepyrene constituting the majority of total POM emissions.[5,7,10-12]

Total particulate and gaseous POM emissions from ESP-controlled cyclone utility boilers were found to range from 0.05 to 24.6 pg/J (0.11 to 57.2 lb/10^{12} Btu), with the average being 4.3 pg/J (14.2 lb/10^{12} Btu). The dominant compounds constituting total particulate and gaseous POM emissions were naphthalene, biphenyl, phenanthrene, and trimethyl propenyl naphthalene. Total particulate POM emissions from ESP-controlled cyclone boilers ranged from 0.5 to 3.2 pg/J (1.2 to 7.4 lb/10^{12} Btu), with pyrene, benzo(e)pyrene, benzo(a)pyrene, and benzo(g,h,i)perylene constituting the majority of the emissions. The single test of a cyclone boiler controlled by a wet scrubber showed total particulate and gaseous POM emissions to be 7.0 pg/J (16.2 lb/10^{12} Btu). Naphthalene and biphenyl compounds accounted for the bulk of total POM emissions.[7,10-12]

Stoker utility boilers with known multicyclone controls had reported total particulate and gaseous POM emissions ranging from 5.2 to 6.3 pg/J (12.0 to 14.6 lb/10^{12} Btu). The bulk of these emissions consisted of naphthalene and biphenyl compounds. Total particulate POM emissions from stokers equipped with multicyclones ranged from 0.054 to 0.20 pg/J (0.13 to

0.47 lb/10^{12} Btu). The major constituents of total particulate POM emissions were pyrene, fluoranthene, benzo(e)pyrene, and benzo(a)pyrene. The discrepancy between the total particulate POM and the total particulate and gaseous POM emissions levels for multicyclone-controlled stokers in part illustrates the significance of unmeasured gaseous POM emissions in the former case.[5,7,11,12]

Total particulate and gaseous POM emissions from a stoker controlled by a baghouse were found to be 39.6 pg/J (92.1 lb/10^{12} Btu). Naphthalene constituted 97 percent of these emissions.[11]

The available test results for POM emissions from utility boilers indicate that gaseous POM emissions are a significant part of total POM. In all cases where total particulate POM and total particulate and gaseous POM emissions data are available for sources, total particulate and gaseous POM levels are five to ten times higher than total particulate POM alone. Therefore, test procedures only measuring for particulate POM may significantly underestimate POM emissions from utility coal combustion sources.

Industrial Coal Combustion--

Polycyclic organic matter emissions data are available for pulverized coal (Table 7) and stoker (Table 8) type industrial boilers. For pulverized coal units controlled by an ESP, total particulate and gaseous POM ranged from 29.3 to 52.1 pg/J (68 to 121 lb/10^{12} Btu), with benzofluoranthenes, anthracene/phenanthrene, fluoranthene, and chrysene/benz(a)anthracene constituting the bulk of the emissions. Total particulate and gaseous POM emissions from a pulverized coal boiler controlled by a multicyclone/ESP combination were significantly less, 2.8 pg/J (6.6 lb/10^{12} Btu), than the ESP control only tests. Phenanthrene and naphthalene accounted for 93 percent of the total POM emissions from the multicyclone/ESP-controlled unit.[13,14]

TABLE 7. POM EMISSION FACTORS FOR PULVERIZED COAL INDUSTRIAL BOILERS

Boiler Characteristics	Coal Type	Controls Used	Total POM Emission Factor pg/J-heat Input ($lb/10^{12}$ Btu-heat Input)	Reference
Dry Bottom, Watertube	Bituminous	Multicyclones	1.2 (2.8)[a]	5
Watertube	Bituminous	ESP	29.3 (68.0)[b]	13
Wet Bottom	Bituminous	Cyclones/ESP	2.8 (6.6)[c]	13
Dry Bottom, Horizontally-Fired	Bituminous	ESP	52.1 (121)[d]	14

[a] Factor represents primarily particulate POM emissions. Eleven specific POM compounds were analyzed for during these tests. Specific compounds identified were benzo(a)pyrene, pyrene, benzo(e)pyrene, anthracene, and fluoranthene. Fluoranthene, anthracene, and pyrene accounted for 90 percent of total POM emissions.

[b] Factor represents both particulate and gaseous POM emissions. Specific compounds identified were anthracene/phenanthrene, fluoranthene, dibenzothiophene, methylanthracenes/phenanthrenes, dimethylanthracenes/phenanthrenes, methylfluoranthenes/pyrenes, benzo(c)phenanthrene, dimethylbenz(a)anthracenes, methylcholanthrenes, indeno(1,2,3-c,d)pyrene, benzofluoranthenes, dibenz(a,h)anthracene, dibenzopyrenes, and methylchrysenes. The primary constituents of total POM emissions are benzofluoranthenes (38 percent), fluoranthene (18 percent), anthracene/phenanthrene (18 percent), and methylcholanthrenes (10 percent).

[c] Factor represents both particulate and gaseous POM emissions. Fifty-six specific POM compounds were analyzed for during these tests. Specific compounds identified were biphenyl, phenanthrene, pyrene, naphthalene, and benzo(g,h,i)perylene. Phenanthrene and naphthalene constituted 93 percent of total POM emissions.

[d] Factor represents both particulate and gaseous POM emissions. Specific compounds identified were dibenzothiophene, anthracene/phenanthrene, methylanthracenes/phenanthrenes, dimethylanthracenes/phenanthrenes, fluoranthene, pyrene, methyl fluoranthenes/pyrenes, benzo(c)phenanthrene, chrysene/benz(a)anthracene, dimethylbenz(a)anthracenes, benzofluoranthenes, benzopyrenes/perylene, methylcholanthrenes, indeno(1,2,3-c,d)-pyrene, dibenz(a,h)anthracene, dibenzo(c,g)carbazole, dibenzopyrenes, methylchrysenes, anthracene/benzo(g,h,i)perylene. The primary constituents of total POM emissions are chrysene/benz(a)anthracene (41 percent), benzofluoranthenes (22 percent), fluoranthene (11 percent), and anthracene/phenanthrene (11 percent).

TABLE 8. POM EMISSION FACTORS FOR COAL-FIRED, STOKER INDUSTRIAL BOILERS

Boiler Characteristics	Coal Type	Controls Used	Total POM Emission Factor pg/J-heat Input ($lb/10^{12}$ Btu-heat Input)	Reference
Spreader Stoker	a	Multicyclones	1.3 (2.97)[b,c]	5
Underfeed Stoker	a	None	84.7 (197)[b,d]	5
Chain Grate Stoker	a	None	1.18 (2.7)[b,e]	5
Spreader Stoker	Bituminous	Cyclones/ESP	178 (413)[f]	13
Spreader Stoker	Bituminous/ Subbituminous	None	5.9 (13.7)[g,h]	15
Spreader Stoker	Bituminous	None	4.3 (10.0)[g,i]	15
Mass-Fired Overfeed Stoker	Bituminous	None	14.2 (32.9)[g,j]	15

[a] Data not reported in the available literature.

[b] Factor represents primarily particulate POM emissions. Eleven specific POM compounds were analyzed for during these tests.

[c] Specific compounds identified were benzo(a)pyrene, pyrene, benzo(e)pyrene, coronene, and fluoranthene. Pyrene, benzo(e)pyrene, and fluoranthene constitute 96 percent of total POM emissions.

[d] Specific compounds identified were benzo(a)pyrene, pyrene, benzo(e)pyrene, perylene, coronene, fluoranthene, phenanthrene, anthracene, anthanthrene, and benzo(g,h,i)perylene. The primary constituents of total POM emissions are fluoranthene (42 percent), pyrene (18 percent), benzo(a)pyrene (11 percent), phenanthrene (11 percent), and benzo(e)pyrene (9 percent).

[e] Specific compounds identified were benzo(a)pyrene, pyrene, benzo(e)pyrene, and fluoranthene. Fluoranthene and pyrene accounted for 87 percent of total POM emissions.

[f] Factor represents both particulate and gaseous POM emissions. Fifty-six specific POM compounds were analyzed for during these tests. Specific compounds identified were naphthalene, phenanthrene, fluoranthene, pyrene, chrysene, benzo(a)pyrene, o-phenylene pyrene, and benzo(g,h,i)perylene. The primary constituents of total POM emissions were phenanthrene (31 percent), pyrene (30 percent), chrysene (16 percent), and naphthalene (11 percent).

[g] Factor represents both particulate and gaseous POM emissions. Twenty-one specific POM compounds were analyzed for during these tests. Generally, the majority of POM was measured in a gaseous as opposed to particulate phase.

[h] This factor is the average of single emission tests on three boilers. For the three tests, total POM factors ranged from 0.55 to 13.5 pg/J (1.28 to 31.3 $lb/10^{12}$ Btu). The primary constituents of total POM emissions were phenanthrene (64 percent), fluoranthene (17 percent), and pyrene (6 percent).

[i] This factor is the average of single emission tests on three boilers. For the three tests, total POM factors ranged from 0.52 to 18.7 pg/J (1.21 to 43.4 $lb/10^{12}$ Btu). The primary constituents of total POM emissions were phenanthrene (51 percent), methylanthracenes/phenanthrenes (23 percent), and fluoranthene (11 percent).

[j] This factor is the average of single emission tests on five boilers. For the five tests, total POM factors ranged from 0.56 to 90.3 pg/J (1.3 to 210 $lb/10^{12}$ Btu). The primary constituents of total POM emissions were phenanthrene (32 percent), anthracene (30 percent), and fluoranthene (30 percent).

The single value available for total particulate POM emissions from a multicyclone-controlled pulverized coal boiler [1.2 pg/J (2.8 lb/10^{12} Btu)] further confirms the significance of gaseous POM emissions from combustion sources.[5] Although only controlled by a multicyclone, total particulate POM emissions are very low compared to the ESP-controlled total particulate and gaseous POM case indicating probably a large loss of gaseous POM through the multicyclone and some loss of gaseous POM from the ESP.

The POM emission factor data for stoker industrial boilers are conflicting and inconsistent in relation to expected POM emission trends under the given control scenarios. Uncontrolled total particulate POM emissions from stokers were found to range from 1.18 to 84.7 pg/J (2.97 to 197 lb/10^{12} Btu). However, uncontrolled total particulate and gaseous POM emissions only ranged from 4.3 to 14.2 pg/J (10.0 to 32.9 lb/10^{12} Btu). The significance of gaseous POM emissions can not be observed from these data. The inconsistency of the results are further compounded when the number of POM compounds analyzed for in each data set is considered. The total particulate and gaseous POM tests analyzed for twice as many compounds as the total particulate POM tests. The single data point for a controlled total particulate and gaseous POM emissions case lessens the ability to draw conclusions or establish trends from the stoker boiler POM data in Table 8. Total particulate and gaseous POM emissions from a multicyclone/ESP-controlled stoker were found in one case to be 178 pg/J (413 lb/10^{12} Btu). Reconciling this data point with an uncontrolled total particulate POM emission factor of 1.18 pg/J (2.7 lb/10^{12} Btu) or with an uncontrolled total particulate and gaseous POM emission factor of 4.3 pg/J (10.0 lb/10^{12} Btu) is not possible with the available information from the source tests.[5,13,15]

Commercial and Residential Coal Combustion--

The total POM emission factor data for commercial and residential boilers given in Table 9 span a wide range from 4.2 to 36,392 pg/J (9.7 to 84,561 lb/10^{12} Btu). Uncontrolled total particulate POM emissions from commercial and residential units (primarily stokers) range from 5.9 to

TABLE 9. UNCONTROLLED POM EMISSION FACTORS FOR COMMERCIAL AND RESIDENTIAL COAL-FIRED BOILERS

Boiler Type	Coal Type	Total POM Emission Factor pg/J-heat Input (lb/10^{12} Btu-heat Input)	Reference
Underfeed Stoker	a	5.9 (13.8)[b,c]	5
Cast Iron Underfeed Stoker	a	90.4 (210)[b,d]	5
Hand Stoked Hot Air Furnace	a	3,779 (8,780)[b,e]	5
Underfeed Stoker	a	1,414 (3,285)[b,f]	12
Underfeed Stoker	a	893 (2,076)[b,g]	12
Underfeed Stoker Hot Air Furnace	a	810 (1,881)[b,h]	12
Underfeed Stoker Hot Air Furnace	a	1 (432)[b,i]	12
Hand Stoked Hot Air Furnace	a	14,116 (32,800)[b,j]	12
Hand Stoked Hot Air Furnace	a	36,392 (84,561)[b,k]	12
Underfeed Stoker	Bituminous	1,501 (3,480)[l]	16
Underfeed Stoker	Bituminous	170 (395)[l]	16
Underfeed Stoker	High-Volatile Bituminous	5,767 (13,400)[l,m]	17
Underfeed Stoker	High-Volatile Bituminous	5,509 (12,800)[l,m]	17
Underfeed Stoker	High-Volatile Bituminous	1,549 (3,600)[l,m]	17
Underfeed Stoker	High-Volatile Bituminous	826 (1,920)[l,m]	17
Underfeed Stoker	High-Volatile Bituminous	594 (1,380)[l,m]	17
Underfeed Stoker	High-Volatile Bituminous	363 (844)[l,m]	17
Underfeed Stoker	Subbituminous	848 (1,970)[l,m]	17
Underfeed Stoker	Subbituminous	925 (2,150)[l,m]	17
Underfeed Stoker	Subbituminous	283 (658)[l,m]	17
Underfeed Stoker	Subbituminous	693 (1,610)[l,m]	17
Underfeed Stoker	Subbituminous	607 (1,410)[l,m]	17
Underfeed Stoker	Low-Volatile Bituminous	1,743 (4,050)[l,n]	17
Underfeed Stoker	Processed Lignite Char	161 (374)[l,o]	17
Underfeed Stoker	Anthracite	68.4 (159)[l,o]	17
Underfeed Stoker	Anthracite	9.6 (22.2)[l,o]	17
Underfeed Stoker	Bituminous	7,746 (18,000)[p]	18
Underfeed Stoker	Bituminous	860 (2,000)[p]	18

TABLE 9. UNCONTROLLED POM EMISSION FACTORS FOR COMMERCIAL AND RESIDENTIAL COAL-FIRED BOILERS (Continued)

Boiler Type	Coal Type	Total POM Emission Factor pg/J-heat Input (lb/10^{12} Btu-heat Input)	Reference
Magazine Feed	Anthracite	21.3 (49.4)^{q,r}	19
Magazine Feed	Anthracite	4.2 (9.7)^{q,s}	19
Hand Stoked	Anthracite	24.8 (57.5)^{q,t}	19
Magazine Feed	Bituminous	3,526 (8,177)^{q,u}	19
Magazine Feed	Bituminous	1,135 (2,632)^{q,v}	19
Hand Stoked	Bituminous	1,843 (4,274)^{q,w}	19

[a] Data not reported in the available literature.

[b] Factors represent primarily particulate POM emissions. Ten specific POM compounds were analyzed for during these tests.

[c] Specific compounds identified were benzo(a)pyrene, pyrene, benzo(e)pyrene, phenanthrene, and fluoranthene. The primary constituents of total POM emissions were fluoranthene (51 percent), pyrene (27 percent), and phenanthrene (16 percent).

[d] Specific compounds identified were benzo(a)pyrene, pyrene, benzo(e)pyrene, benzo(g,h,i)perylene, coronene, phenanthrene, and fluoranthene. The primary constituents of total POM emissions were fluoranthene (50 percent), phenanthrene (31 percent), and pyrene (8 percent).

[e] Specific compounds identified were benzo(a)pyrene, pyrene, benzo(e)pyrene, benzo(g,h,i)perylene, coronene, perylene, anthanthrene, anthracene, phenanthrene, and fluoranthene. The primary constituents of total POM emisisons were phenanthrene (25 percent), fluoranthene (25 percent), pyrene (15 percent), anthracene (10 percent), and benzo(a)pyrene (10 percent).

[f] All ten POM compounds listed in footnote e were also identified in these emissions. The primary constituents of total POM emissions were phenanthrene (41 percent), fluoranthene (22 percent), pyrene (20 percent), and anthracene (5 percent).

[g] All ten POM compounds listed in footnote e except coronene were also identified in these emissions. The primary constituents of total POM emissions were phenanthrene (37 percent), pyrene (20 percent), fluoranthene (16 percent), and benzo(a)pyrene (9 percent).

[h] All ten POM compounds listed in footnote e were also identified in these emissions. The primary constituents of total POM emissions were fluoranthene (37 percent), phenanthrene (20 percent), pyrene (19 percent), and benzo(a)pyrene (8 percent).

[i] All ten POM compounds listed in footnote e except coronene and anthanthrene were also identified in these emissions. The primary constituents of total POM emissions were fluoranthene (39 percent), phenanthrene (26 percent), and pyrene (23 percent).

[j] All ten POM compounds listed in footnote e were also identified in these emissions. The primary constituents of total POM emissions were fluoranthene (29 percent), pyrene (18 percent), phenanthrene (15 percent), benzo(a)pyrene (11 percent), and benzo(g,h,i)perylene (9 percent).

[k] All ten POM compounds listed in footnote e were also identified in these emissions. The primary constituents of total POM emissions were fluoranthene (29 percent), pyrene (24 percent), phenanthrene (20 percent), and benzo(a)pyrene (9 percent).

[l] Factor represents both particulate and gaseous POM emissions. Twenty-two specific POM compounds were analyzed for during these tests. The compounds analyzed for included anthracene, phenanthrene, methyl anthracenes, fluoranthene, benzo(c)phenanthrene, chrysene, benz(a)anthracene, methyl chrysenes, 7,12-dimethylbenz(a)anthracene, benzofluoranthenes, benzo(a)pyrene, benzo(e)pyrene, perylene, 3-methylcholanthrene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, dibenzo(c,g)carbazole, dibenzo(a,i)pyrene, and dibenzo(a,h)pyrene.

TABLE 9. UNCONTROLLED POM EMISSION FACTORS FOR COMMERCIAL AND RESIDENTIAL COAL-FIRED BOILERS (Continued)

---

[m] The predominant POM compounds occurring during high-volatile bituminous coal combustion were anthracene, phenanthrene, methyl anthracenes, fluoranthene, pyrene, and methyl pyrene/fluoranthene.

[n] The predominant POM compounds occurring during low-volatile bituminous coal combustion were anthracene, phenanthrene, methyl anthracenes, fluoranthene, chrysene/benz(a)anthracene, methyl chrysenes, pyrene, and methyl pyrene/fluoranthene.

[o] The predominant POM compounds occurring during processed lignite char and anthracite coal combustion were anthracene, phenanthrene, methyl anthracenes, fluoranthene, pyrene, chrysene/benz(a)anthracene, and benzofluoranthenes.

[p] Factor represents both particulate and gaseous POM emissions. Individual POM compounds measured were not identified.

[q] Factor represents both particulate and gaseous POM emissions. Eighteen specific POM compounds were analyzed for during these tests.

[r] The primary constituents of total POM emissions were phenanthrene (23 percent), fluoranthene (18 percent), pyrene (13 percent), chrysene (12 percent), benzo(a)anthracene (11 percent), and naphthalene (11 percent). The test was conducted under high burn rate conditions.

[s] The primary constituents of total POM emissions were fluoranthene (26 percent), phenanthrene (25 percent), pyrene (15 percent), chrysene (6 percent), acenaphthene (4 percent), acenaphthylene (4 percent), benzo(a)anthracene (4 percent), and benzo(k)fluoranthene (4 percent). The test was conducted under low burn rate conditions.

[t] The primary constituents of total POM emissions were naphthalene (31 percent), phenanthrene (20 percent), acenaphthylene (14 percent), fluoranthene (10 percent), pyrene (8 percent), and chrysene (3 percent). The test was conducted under moderate burn rate conditions.

[u] The primary constituents of total POM emissions were acenaphthylene (24 percent), naphthalene (18 percent), phenanthrene (17 percent), fluoranthene (8 percent), anthracene (5 percent), pyrene (5 percent), fluorene (5 percent), and benzo(k)fluoranthene (4 percent). The test was conducted under high burn rate conditions.

[v] The primary constituents of total POM emissions were naphthalene (19 percent), phenanthrene (16 percent), anthracene (9 percent), benzo(k)fluoranthene (8 percent), fluorene (8 percent), fluoranthene (7 percent), pyrene (6 percent), benzo(a)pyrene (5 percent), and benzo(a)anthracene (4 percent). The test was conducted under low burn rate conditions.

[w] The primary constituents of total POM emissions were naphthalene (11 percent), acenaphthylene (11 percent), phenanthrene (11 percent), benzo(k)fluoranthene (9 percent), fluoranthene (9 percent), fluorene (7 percent), pyrene (6 percent), benzo(a)anthracene (6 percent), anthracene (5 percent), indeno(1,2,3-c,d)perylene (5 percent), and chrysene (5 percent). The test was conducted under moderate burn rate conditions.

36,392 pg/J (13.8 to 84,561 lb/10^{12} Btu), with the average factor being 6,410 pg/J (14,893 lb/10^{12} Btu). Uncontrolled total particulate and gaseous POM emissions range from 4.2 to 7,746 pg/J (9.7 to 18,000 lb/10^{12} Btu), with the average emission factor being 1471 pg/J (3412 lb/10^{12} Btu).[5,12,17-19] As with the industrial coal combustion data, the reported total POM emission data for commercial and residential boilers are inconsistent given the expected significance of gaseous POM emissions and the fact that the total particulate and gaseous POM emissions data examined twice the number of POM compounds covered in the total particulate only tests.

The primary constituents of uncontrolled POM emissions from commercial and residential boilers burning coal are fluoranthene, phenanthrene, anthracene, pyrene, and chrysene/benz(a)anthracene.[5,12,17-19]

Residual Oil Combustion--

Emission factors for POM from residual oil combustion sources are presented in Table 10. Total particulate and gaseous POM emissions from uncontrolled residual oil combustion range from 0.029 to 33.3 pg/J (0.066 to 77.3 lb/10^{12} Btu), with the average being 3.2 pg/J (7.4 lb/10^{12} Btu). If the upper value of the range (33.3 pg/J) is excluded, the average emission factor becomes 0.70 pg/J (1.6 lb/10^{12} Btu). The principal constituents of total particulate and gaseous POM emissions are naphthalene, biphenyl, phenanthrene, anthracene, and fluoranthene. Uncontrolled total particulate POM emission factor data had less variability and only ranged from 0.95 to 4.4 pg/J (2.2 to 10.2 lb/10^{12} Btu), with the average being 2.4 pg/J (5.7 lb/10^{12} Btu). Total particulate POM emissions consisted primarily of phenanthrene, fluoranthene, methyl anthracenes/phenanthrenes, and pyrene.[5,11,13,16,20]

Only one POM emission factor was identified for controlled emissions from residual oil combustion. Total particulate and gaseous POM emissions from a cyclone-controlled utility boiler were 2.5 pg/J (5.8 lb/10^{12} Btu). Naphthalene and biphenyl constituted 100 percent of this emission factor.[11]

TABLE 10. POM EMISSION FACTORS FOR RESIDUAL OIL COMBUSTION

Boiler Type	Boiler Application	Controls Used	Total POM Emission Factor pg/J-heat Input (lb/10^{12} Btu-heat Input)	Reference
Tangential-Fired	Electric Utility	None	33.3 (77.3)[a,b]	11
Wall-Fired	Electric Utility	None	0.56 (1.3)[a,c]	11
Wall-Fired	Electric Utility	None	12.3 (28.6)[a,d]	11
Wall-Fired	Electric Utility	None	0.45 (1.0)[a,e]	11
Wall-Fired	Electric Utility	None	2.6 (5.9)[a,f]	11
Face-Fired	Electric Utility	None	2.1 (4.8)[g]	20
Not Reported	Electric Utility	None	4.4 (10.2)[h]	20
Face-Fired	Electric Utility	None	0.32 (0.75)[i]	20
Face-Fired	Electric Utility	None	0.42 (0.98)[j]	20
Tangential-Fired	Electric Utility	Cyclones	2.5 (5.8)[a,k]	11
Not Reported	Electric Utility	None	0.029 - 0.89 (0.066 - 2.1)[l]	21
Steam Atomized Watertube	Industrial Heating	None	2.3 (5.4)[m]	5
Watertube	Industrial Heating	None	0.63 (1.5)[a,n]	13
Scotch Marine	Commercial Heating	None	0.95 (2.2)[o]	16

[a] Factor represents both particulate and gaseous POM emissions. Fifty-six specific POM compounds were analyzed for during these tests.

[b] Specific compounds identified were naphthalene and biphenyl. Naphthalene accounted for 96 percent of total POM emissions.

[c] Specific compounds identified were 2-ethyl-1,1-biphenyl and naphthalene. 2-Ethyl-1,1-biphenyl accounted for 64 percent of total POM emissions and naphthalene 36 percent.

[d] Specific compounds identified were naphthalene and biphenyl. Naphthalene constituted 94 percent of total POM emissions and biphenyl 6 percent.

[e] Specific compounds identified were 2-ethyl-1,1-biphenyl and 1,2,3-trimethyl-4-propenyl naphthalene, each of which constituted 50 percent of total POM emissions.

[f] Specific compounds identified were naphthalene, phenanthridine, dibenzothiophene, anthracene/phenanthrene, fluoranthene, pyrene, chrysene/benz(a)anthracene, benzopyrene/perylenes, and tetramethyl phenanthrene. The primary constituents of total POM emissions were naphthalene (67 percent), anthracene/phenanthrene (8 percent), fluoranthene (7 percent), pyrene (7 percent), and tetramethyl phenanthrene (4 percent).

[g] Factor represents primarily particulate POM emissions. Specific compounds identified were phenanthrene, anthracene, methyl anthracenes/phenanthrenes, fluoranthrene, pyrene, methyl pyrene/fluoranthene, benzo(c)phenanthrene, benzo(a)anthracene, chrysenes, methyl chrysenes, benzofluoranthenes, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno-pyrene, coronene, and benzo(g,h,i)perylene. The primary constituents of total POM emissions were phenanthrene (16 percent), methyl anthracenes/phenanthrenes (13 percent), fluoranthene (8 percent), and pyrene (7 percent).

TABLE 10. POM EMISSION FACTORS FOR RESIDUAL OIL COMBUSTION (Continued)

---

[h] Factor represents primarily particulate POM emissions. Specific compounds identified were phenanthrene, anthracene, methyl anthracenes/phenanthrenes, fluoranthene, pyrene, methyl pyrene/fluoranthene, benzo(c)phenanthrene, benzo(a)anthracene, chrysenes, benzofluoranthenes, benzo(e)pyrene, and benzo(a)pyrene. The primary constituents of total POM emissions were phenanthrene (51 percent), fluoranthene (14 percent), benzo(g,h,i)perylene (9 percent), and methyl anthracenes/phenanthrenes (7 percent).

[i] Factor represents both particulate and gaseous POM emissions. Specific compounds identified were phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, and chrysene. The primary constitutents of total POM emissions were phenanthrene (35 percent), anthracene (31 percent), fluoranthene (14 percent), and pyrene (14 percent). Approximately 63 percent of total POM emissions were measured in the gaseous phase.

[j] Factor represents both particulate and gaseous POM emissions. Specific compounds identified were phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, and chrysene. The primary constituents of total POM emissions were phenanthrene (34 percent), anthracene (31 percent), fluoranthene (15 percent), and pyrene (12 percent). Approximately 65 percent of total POM emissions were measured in the gaseous phase.

[k] Specific compounds identified were naphthalene and biphenyl. Naphthalene constituted 72 percent of total POM emissions and biphenyl 28 percent.

[l] Factor represents both particulate and gaseous POM emissions. Twenty-one specific POM compounds were analyzed for during these tests. The principal constituents of total POM emissions were anthracene/phenanthrene (53 percent), fluoranthene (17 percent), pyrene (15 percent), and methyl anthracenes (5 percent).

[m] Factor represents primarily particulate POM emissions. Specific compounds identified were benzo(a)pyrene, pyrene, phenanthrene, and fluoranthene. Phenanthrene constituted about 75 percent of total POM emissions, pyrene 12 percent, and fluoranthene 11 percent.

[n] This factor is for biphenyl emissions only. No other POM compounds were measured during these tests.

[o] This factor is for benzo(a)pyrene only. No other POM compounds were measured during these tests.

Distillate Oil Combustion--

For distillate oil combustion (Table 11), emission factors are only available for total particulate POM emissions and not total particulate and gaseous emissions. Uncontrolled emissions range from 0.12 to 17.7 pg/J (0.28 to 41.2 $lb/10^{12}$ Btu), with the average being 9.7 pg/J (22.5 $lb/10^{12}$ Btu). Fluoranthene, pyrene, phenanthrene, benzo(a)pyrene, and anthracene account for the bulk of distillate oil combustion POM emissions. Overall, POM emissions from distillate oil combustion appear to run slightly higher than emissions from residual oil combustion. One possible cause of this apparent trend would be that distillate oil combustion sources have less efficient combustion systems than larger, residual oil combustion sources. Less efficient combustion promotes increased POM formation and release.[5]

Industrial and Commercial Wood Combustion--

Polycyclic organic matter emission factors for industrial and commercial wood-fired boilers are presented in Tables 12 and 13. Expressed in terms of mass of fuel burned (inclusive of moisture), uncontrolled total particulate and gaseous POM emissions from wood-fired boilers have been shown to range from 10 to 1150 mg/kg (average of 214 mg/kg). In Table 12, uncontrolled total particulate and gaseous POM emissions, expressed in terms of mass of dry fuel burned, range from 0.22 to 4.23 mg/kg (average of 1.7 mg/kg). Data are not available to readily explain the wide variance between the emission factors for these seemingly similar emission sources. The predominant POM compounds measured in uncontrolled POM emissions from wood-fired boilers were naphthalene, phenanthrene, anthracene, pyrene, benzo(a)anthracene, benzo(b and k)fluoranthene, and benzo(a and e)pyrene.[13,16,22,23]

Uncontrolled total particulate and gaseous emissions from wood-fired boilers (Table 12), expressed in terms of heat input, reportedly range from 10.1 to 26,299 pg/J (23.4 to 60,993 $lb/10^{12}$ Btu), with the average emission factor being 7,224 pg/J (16,752 $lb/10^{12}$ Btu). Naphthalene, phenanthrene,

TABLE 11. UNCONTROLLED POM EMISSION FACTORS FOR DISTILLATE OIL COMBUSTION

Boiler Type	Boiler Application	Total POM Emission Factor pg/J-heat input ($lb/10^{12}$ Btu-heat input)[a]	Reference
Watertube	Process Heating	<0.12 (<0.28)[b]	5
Scotch Marine	Hospital Heating	17.7 (41.2)[c]	5
Cast Iron Sectional	Home Heating	<14.9 (<34.6)[d]	5
Hot Air Furnace	Home Heating	<0.14 (<0.33)[e]	5
Hot Air Furnace	Home Heating	<15.4 (<35.9)[f]	5

---

[a] Factors represent primarily particulate POM emissions. Eleven specific POM compounds were analyzed for during these tests.

[b] Specific compounds identified were benzo(a)pyrene, pyrene, and fluoranthene. Fluoranthene accounted for 45 percent of total POM emissions, pyrene 39 percent, and benzo(a)pyrene 16 percent.

[c] Specific compounds identified were benzo(a)pyrene, pyrene, benzo(g,h,i)-perylene, coronene, anthracene, phenanthrene, and fluoranthene. Primary constituents of total POM emissions were pyrene (33 percent), anthracene (21 percent), phenanthrene (19 percent), and coronene (11 percent).

[d] Specific compounds identified were benzo(a)pyrene, pyrene, phenanthrene, and fluoranthrene. Phenanthrene constituted 57 percent of total POM emissions, fluoranthene 32 percent, and pyrene 11 percent.

[e] Specific compounds identified were benzo(a)pyrene, pyrene, and fluoranthene. Fluoranthene constituted 50 percent of total POM emissions, benzo(a)pyrene 40 percent, and pyrene 10 percent.

[f] Specific compounds identified were benzo(a)pyrene, pyrene, and fluoranthene. Fluoranthene accounted for 92 percent of total POM emissions, pyrene 7 percent, and benzo(a)pyrene 1 percent.

TABLE 12. POM EMISSION FACTORS FOR INDUSTRIAL AND COMMERCIAL WOOD-FIRED BOILERS

Reference	Total POM Emission Factor[a] Range	Total POM Emission Factor[a] Mean	Source Type	Fuel Type	Controls Used
22	80 - 1,150 mg/kg[b]	620 mg/kg[b]	Industrial Down-Draft Boiler	White Oak	None
23	10 - 120 mg/kg[b,c]	65 mg/kg[b,c]	Industrial Stick Burner Boiler	White Oak and Mixed Logs	None
23	20 - 170 mg/kg[b,d]	83 mg/kg[b,d]	Industrial Stick Burner Boiler	White Oak and Mixed Logs	None
23	50 - 110 mg/kg[b,e]	87 mg/kg[b,e]	Industrial Stick Burner Boiler	White Oak and Mixed Logs	None
13	ND - 0.047 pg/J[b,f]	0.014 pg/J[b,f]	Industrial Spreader Stoker Boiler	Bark	Cyclones
13	ND - 0.067 pg/J[b,f]	0.022 pg/J[b,f]	Industrial Spreader Stoker Boiler	Bark	Cyclones/ Wet Scrubber
13	---	27 pg/J[b,g,h]	Industrial Underfeed Stoker Boiler	Not Reported	None
13	---	783 pg/J[b,g,i]	Industrial Underfeed Stoker Boiler	Not Reported	Wet Scrubber
13	---	118 pg/J[b,g,j]	Industrial Underfeed Stoker Boiler	Not Reported	Wet Scrubber
13	---	10.1 pg/J[b,g,k]	Industrial Underfeed Stoker Boiler	Not Reported	None
13	---	2,558 pg/J[b,g,l]	Industrial Underfeed Stoker Boiler	Not Reported	None
16	---	26,299 pg/J[b,g,m]	Commercial Underfeed Stoker Boiler	Not Reported	None
24	1.2 - 3.4 mg/kg[b,n,o]	1.9 mg/kg[b,n,o]	Industrial Hot Water Boiler	Hardwood Chips	Multiclone
24	---	15 mg/kg[b,n,p]	Industrial Hot Water Boiler	Peat	Multiclone

[a] mg/kg emission factors mean mg of POM emissions per kg of wood burned. pg/J emission factors mean pg of POM emissions per J of heat input to the boiler.

[b] Factor represents both particulate and gaseous POM emissions.

[c] Factor applies to the steady-state portion of the test.

[d] Factor applies to the smoldering fire portion of the test.

[e] Factor applies to the cold start portion of the test.

[f] Factor applies to benzo(a)pyrene emissions only.

[g] Fifty-six specific POM compounds were analyzed for during these tests.

[h] Reported value is for naphthalene only.

[i] Specific compounds identified were naphthalene, biphenyl, fluorene, phenanthrene, pyrene, fluoranthene, benzo(g,h,i)fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, and indeno(1,2,3-c,d)fluoranthene. The primary constituents of total POM emissions were naphthalene (65 percent), phenanthrene (12 percent), fluoranthene (9 percent), and pyrene (6 percent).

TABLE 12. POM EMISSION FACTORS FOR INDUSTRIAL AND COMMERCIAL WOOD-FIRED BOILERS (Continued)

[j] Specific compounds identified were naphthalene, biphenyl, phenanthrene, and fluoranthene. Naphthalene constituted 95 percent of total POM emissions.

[k] Specific compounds identified were naphthalene, phenanthrene, fluoranthene, and pyrene. Naphthalene constituted 82 percent of total POM emissions and phenanthrene 13 percent.

[l] Specific compounds identified were naphthalene, biphenyl, phenanthrene, fluoranthene, pyrene, chrysene, benzo(a)pyrene, and benzo(b)fluoranthene. The primary constituents of total POM emissions were phenanthrene (49 percent), naphthalene (28 percent), fluoranthene (6 percent), and pyrene (5 percent).

[m] Specific compounds identified were naphthalene, biphenyl, fluorene, phenanthrene, methyl phenanthrene, phenyl naphthalene, fluoranthene, pyrene, methyl pyrene, benzo(g,h,i)fluoranthene, chrysene, benzo(a)anthracene, benzo(a)pyrene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, dibenzo(a,i)pyrene, benzo(c)fluoranthene, and methyl benzo(a)anthracene. The primary constituents of total POM emissions were phenanthrene (17 percent), benzo(a)pyrene (14 percent), naphthalene (13 percent), pyrene (9 percent), benzo(g,h,i)perylene (9 percent), fluoranthene (9 percent), benzo(g,h,i)fluoranthene (5 percent), and biphenyl (4 percent).

[n] Emission factors expressed as mg POM/kg of dry fuel burned. Sixteen specific POM compounds were analyzed for during these tests.

[o] Phenanthrene, fluoranthene, and pyrene account for about 77 percent of total POM emissions.

[p] The primary constituents of total POM emissions are phenanthrene (42 percent), fluoranthene (18 percent), pyrene (15 percent), chrysene/triphenylene (5 percent), and benzo(b and k)fluoranthene (5 percent).

TABLE 13. POM SPECIES EMISSION FACTORS FOR CONTRO

POM Compound								Test Site
	K1	K2	K3	EA1	EA2	EA3	EA4	BP1
Naphthalene	1.45	1.79	2.17	1.11	3.32	0.26	0.67	0.083
Biphenyl	c	c	c	c	c	0.53	c	c
Fluorene	d	d	d	d	d	d	d	d
Phenanthrene	0.044	d	0.21	d	d	c	d	d
Anthracene	0.007	0.085	0.29	d	d	0.006	d	d
Carbazole	d	d	d	d	d	d	d	d
1-Methylphenanthrene	d	d	d	d	d	d	0.016	0.038
9-Methylanthracene	c	c	c	0.017	d	d	0.008	c
Fluoranthene	c	d	c	d	d	c	0.005	d
Pyrene	d	0.060	d	d	d	0.045	0.072	d
Benzo(a)anthracene	d	0.032	0.26	0.003	d	0.001	0.01	d
Chrysene	d	d	0.025	d	d	0.002	d	d
Benzo(b)fluoranthene[e]	0.038	0.044	0.013	0.006	d	d	d	d
Benzo(k)fluoranthene					d	d	d	d
7,12-dimethylbenz(a)anthracene	d	d	d	d	d	d	d	d
Benzo(e)pyrene	0.013	0.029	0.033	d	d	d	d	d
Benzo(a)pyrene	0.026	0.018	0.017	0.005	d	0.001	d	d
Perylene	d	d	d	d	d	d	d	d
3-Methylcholanthene	d	d	d	d	d	0.002	d	d
Indeno(1,2,3-c,d)pyrene	d	d	d	d	d	0.006	d	d
Dibenz(a,h)anthracene	d	d	0.036	d	d	d	d	d
Benzo(g,h,i)perylene	0.025	d	0.060	d	d	d	d	d
Total POM	1.6	2.06	3.1	1.14	3.32	0.86	0.79	0.12

---

[a] See Table 14 for a description of each test site.

[b] Emission factors represent particulate and gaseous POM emissions. Twenty-two specific POM compounds were analyzed for during these tests.

[c] Compound peak obscured by aliphatic peak.

[d] Compound not detected.

[e] Peak resolution not sufficient to differentiate these two compounds. Value equals the sum of both species.

[f] National Bureau of Standards match not possible for peak identification due to low level of compound or interference.

S FOR CONTROLLED AND UNCONTROLLED WOOD-FIRED INDUSTRIAL BOILERS[25,26]

Test Sites[a]/POM Emission Factors (mg/kg Dry Wood Burned)[b]													
BP1	BP2	HH1	HH2	HH3	SF1	SF2	SF3	EL1	EL2	WW1	WW2	WW3	Mean Emission Factor
0.083	).012	3.19	3.0	2.03	0.056	0.92	0.65	0.46	3.8	0.80	0.41	0.087	1.31
c	c	c	0.14	c	c	c	c	c	c	c	c	d	---
d	d	0.034	0.065	0.013	d	d	0.27	d	d	0.15	0.23	0.25	0.051
d	0.003	0.050[e]	0.015	0.044[e]	0.088	d	d	0.065	0.012	0.45	0.62	0.55	0.11
d	d		d		d	d	d	0.029	0.29	0.13	0.22	0.22	0.064
d	d	d	d	d	d	d	d	d	d	d	d	0.009	0.0004
0.038	d	d	d	d	d	d	d	d	d	d	d	d	0.003
c	d	d	0.014	d	d	d	d	0.026	c	d	d	c	0.003
d	d	c	c	c	d	d	d	d	0.13	c	d	0.009	0.007
d	0.004	c	0.036	0.14	d	0.042	d	0.038	d	0.071	d	c	0.025
d	d	0.017	0.009	d	0.075	d	d	0.016	d	0.078	0.011	0.008	0.026
d	d	0.11	0.010	d	d	d	d	d	d	d	0.005	d	0.008
d	d	0.019[e]	0.020[e]	0.033	d	d	d	d	d	d	d	0.020	0.010
d	d			0.006	d	d	d	d	d	d	d	d	0.010
d	d	d	d	d	d	d	d	d	d	d	d	d	0
d	d	0.002	0.005	0.007	d	d	d	d	d	0.016	0.028	0.034	0.008
d	d	0.002	0.004	0.010	d	d	d	d	d	0.015	0.020	0.024	0.007
d	d	d	d	d	d	d	d	d	d	d	d	d	0
d	d	d	d	d	d	d	d	d	d	d	d	d	0
d	d	0.008	0.026	d	d	d	d	d	d	d	d	d	0.002
d	d	d	d	d	d	d	d	d	d	f	d	d	0.002
d	d	0.034	d	d	d	d	d	d	d	d	d	d	0.006
0.12	0.020	3.47	3.34	2.28	0.22	0.96	0.92	0.64	4.23	0.70	1.55	1.21	2.06

es.

TABLE 14. TEST SITE DESCRIPTIONS FOR THE EMISSION FACTORS GIVEN IN TABLE 13

Test Site	Boiler Type	Fuel Type	Controls Used
K1	HRT[a]	Green Ash	None
K2	HRT[a]	Green Ash	None
K3	HRT[a]	Green Ash	None
EA1	Watertube	Dry Oak	Multicyclone
EA2	Watertube	Dry Oak	Multicyclone
EA3	Watertube	Green Sawdust	Multicyclone
EA4	Watertube	Green Sawdust	Multicyclone
BP1	HRT[a]	Dry Hardwood	Multicyclone
BP2	HRT[a]	Dry Hardwood	Multicyclone
HH1	Underfeed Stoker	Dry Hardwood	Multicyclone
HH2	Underfeed Stoker	Dry Hardwood	Multicyclone
HH3	Underfeed Stoker	Dry Hardwood	Multicyclone
SF1	HRT[a]	Dry Hardwood	None
SF2	HRT[a]	Dry Hardwood	None
SF3	HRT[a]	Dry Hardwood	None
EL1	HRT[a]	Green Pine Sawdust/Bark	None
EL2	HRT[a]	Green Pine Sawdust/Bark	None
WW1	Fluidized Bed	Green Bark	Multicyclone
WW2	Fluidized Bed	Green Bark	Multicyclone
WW3	Fluidized Bed	Green Bark	Multicyclone

[a] Horizontal return tube.

pyrene, fluoranthene, benzo(g,h,i)perylene, and benzo(a)pyrene were the primary components of the uncontrolled POM emissions measured on a heat input basis.[13,16]

Multicyclone-controlled total particulate and gaseous POM emissions from wood boilers (Table 12), expressed on a mass of fuel burned (inclusive of moisture) basis, were found to range from 1.2 to 3.4 mg/kg, with an average emission level being 1.9 mg/kg. Multicyclone-controlled total particulate and gaseous POM emissions, expressed in terms of mass of dry fuel burned (Table 13), ranged from 0.02 to 3.47 mg/kg, with the average being 1.6 mg/kg. The major POM compounds detected in the emissions of multicyclone-controlled wood-fired boilers were phenanthrene, pyrene, fluoranthene, naphthalene, anthracene, and fluorene.[24-26]

As with much of the combustion source POM emissions data, available factors for controlled total particulate and gaseous POM from wood-fired boilers, expressed on a heat input basis, are highly variable and inconsistent. Wet scrubber-controlled total POM emissions have been found to range from 118 to 783 pg/J (274 to 1816 lb/10^{12} Btu), with the average factor being 451 pg/J (1045 lb/10^{12} Btu). Cyclone-controlled total POM emissions from wood-fired boilers have been shown to range from 0 (not detected) to 0.047 pg/J (0 to 0.11 lb/10^{12} Btu), with the average level being 0.014 pg/J (0.03 lb/10^{12} Btu). Given that wet scrubbers should be more effective at controlling POM emissions from wood-fired boilers, the available results reemphasize the unpredictability of POM formation in combustion sources.[13,16]

Available POM emissions data for cyclone/wet scrubber-controlled boilers further confirm the problems inherent in assessing POM emissions from wood-fired combustion sources. Total POM emissions from this type of source have been found to range from 0 (not detected) to 0.067 pg/J (0 to 0.16 lb/10^{12} Btu), with the average being 0.022 pg/J (0.051 lb/10^{12} Btu).[13] These data are slightly greater than the levels from cyclone-controlled sources, which would be unpredicted; however, the cyclone/wet scrubber numbers are four orders of magnitude less than the case for wet scrubber control alone. The gross difference between the wet scrubber only and cyclone/wet scrubber numbers are not reconcilable with the information available in the appropriate source test reports.

Residential Wood Combustion--

Emission factors for POM emissions from wood-fired residential heating sources are presented in Table 15. Disregarding wood type, uncontrolled total particulate and gaseous POM emissions from woodstove units were found to range from 0.096 to 451.2 mg/kg of wood burned. The average uncontrolled emissions level is 189.5 mg/kg. From the literature, it appears that the tests yielding the lower end of the range (0.096 mg/kg) may have not effectively measured gaseous POM emissions. If this data set is excluded from the range, the new range of uncontrolled total particulate and gaseous POM emissions from woodstoves becomes 8.0 to 451.2 mg/kg, with the average factor being 211.6 mg/kg. The principal constituents of POM emissions from residential wood heating sources consistently were naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, 1-methylphenanthrene, and benzofluoranthenes.[3,27-32,34,35]

One set of data were available for baghouse-controlled total particulate and gaseous POM emissions from wood heaters; however, the data are somewhat inconsistent with the uncontrolled wood heater results. The baghouse-controlled POM emission factor range is 148.3 to 155.2 mg/kg, with the average factor being 151.8 mg/kg.[27] Comparing uncontrolled to baghouse-controlled, a more significant difference in average emission factors would be expected. In addition, approximately one-third of the uncontrolled factors were one to one and a half orders of magnitude lower than the controlled values.

Both uncontrolled total particulate POM and uncontrolled total particulate and gaseous POM emission factors are available for fireplaces. Total particulate POM emissions have been found to range from 0.017 to

TABLE 15. POM EMISSION FACTORS FOR WOOD-FIRED RESIDENTIAL HEATING SOURCES

Reference	Total POM Emission Factor mg/kg Fuel Burned	Source Type	Fuel Type
27	155.2[a,b,e]	Fluidized-bed Home Heating Furnace	Pine Wood Chips
27	148.3[a,b,f]	Fluidized-bed Home Heating Furnace	Pine Wood Chips
27	265.8[a,c,g]	Fluidized-bed Home Heating Furnace	Pine Wood Chips
27	341.5[a,c,h]	Fluidized-bed Home Heating Furnace	Pine Wood Chips
27	61.6[a,d,i]	Fluidized-bed Home Heating Furnace	Pine Wood Chips
27	451.2[a,d,j]	Fluidized-bed Home Heating Furnace	Pine Wood Chips
27	8.0[a,d,k]	Cyclone-fired Home Heating Furnace	Pine Wood Chips
27	9.0[a,d,l]	Cyclone-fired Home Heating Furnace	Pine Wood Chips
27	97.5[a,b,m]	Woodstove	Oak Logs
3, 28	4.1[c,n,o]	Woodstove	Unknown
3, 28	8.5[c,n,p]	Woodstove	Unknown
29-32	24.9[c,q,r]	Fireplace	Seasoned Oak
29-32	36.5[c,q,s]	Fireplace	Seasoned Oak
29-32	36.0[c,q,t]	Fireplace	Green Pine
29-32	212.1[c,q,u]	Baffled Woodstove	Seasoned Oak
29-32	371.5[c,q,v]	Baffled Woodstove	Seasoned Pine
29-32	188.5[c,q,w]	Nonbaffled Woodstove	Seasoned Oak

TABLE 15. POM EMISSION FACTORS FOR WOOD-FIRED RESIDENTIAL HEATING SOURCES (Continued)

Reference	Total POM Emission Factor mg/kg Fuel Burned	Source Type	Fuel Type
29-32	318.7[c,q,x]	Nonbaffled Woodstove	Green Pine
29-32	26.5[c,q,y]	Nonbaffled Woodstove	Green Pine
33	0.017[c,z]	Fireplace	Alder Logs
33	0.023[c,z]	Fireplace	Douglas Fir Logs
33	0.017[c,z]	Fireplace	Pine Logs
34	0.096 - 3.36[c,q,aa]	Woodstove	Oak, Maple, and Pine Logs
35	250.7[c,q,bb]	Nonbaffled Woodstove	Oak Brands and Red Oak Logs
35	47.2[c,q,cc]	Nonbaffled, Catalytic Woodstove	Red Oak Logs
35	201.7[c,q,dd]	Nonbaffled Woodstove with Add-on Catalytic Combustor	Red Oak Logs
35	163.2[c,q,ee]	Baffled, Catalytic Woodstove	Red Oak Logs
35	74.7[c,q,ff]	Woodstove with Secondary Combustion	Red Oak Logs

---

[a] Factors represent both particulate and gaseous POM emissions. Twenty-five specific POM compounds were analyzed for during these tests.

[b] Factor represents emissions after control by a baghouse.

[c] Factor represents uncontrolled emissions.

[d] Factor represents the constituents of emissions sampled in the combustion chamber.

[e] The primary constituents of total POM emissions were phenanthrene (29 percent), naphthalene (22 percent), fluoranthene (16 percent), pyrene (11 percent), and fluorene (6 percent).

TABLE 15. POM EMISSION FACTORS FOR WOOD-FIRED RESIDENTIAL HEATING SOURCES (Continued)

---

[f] The primary constituents of total POM emissions were naphthalene (34 percent), fluorene (15 percent), pyrene (13 percent), phenanthrene/anthracene (12 percent), fluoranthene (12 percent), and 1-methylphenanthrene (8 percent).

[g] The primary constituents of total POM emissions were naphthalene (16 percent), pyrene (15 percent, anthracene (12 percent), phenanthrene (12 percent), fluoranthene (10 percent), fluorene (9 percent), and 1-methylphenanthrene (7 percent).

[h] The primary constituents of total POM emissions were pyrene (17 percent), fluoranthene (16 percent), phenanthrene (16 percent), naphthalene (11 percent), benzo(a)pyrene (7 percent), anthracene (6 percent), fluorene (6 percent), and benzo(a)anthracene (5 percent).

[i] The primary constituents of total POM emissions were naphthalene (71 percent), phenanthrene (10 percent), pyrene (6 percent), and fluoranthene (5 percent).

[j] The primary constituents of total POM emissions were naphthalene (72 percent), phenanthrene (11 percent), pyrene (5 percent), and fluoranthene (4 percent).

[k] The primary constituents of total POM emissions were phenanthrene (43 percent), pyrene (17 percent), naphthalene (11 percent), fluoranthene (11 percent), biphenyl (5 percent), and 1-methylphenanthrene (5 percent).

[l] The primary constituents of total POM emissions were naphthalene (61 percent), phenanthrene/anthracene (11 percent), 1-methylphenanthrene (8 percent), fluoranthene (8 percent), and pyrene (6 percent).

[m] The primary constituents of total POM emissions were naphthalene (38 percent), 1-methylphenanthrene (15 percent), biphenyl (12 percent), phenanthrene (10 percent), anthracene (6 percent), and fluorene (5 percent). Factor represents the average results of two emission tests.

[n] Available literature did not indicate whether both particulate and gaseous POM emissions were analyzed for during these tests. The factors presented represent uncontrolled POM emissions.

[o] The primary constituents of total POM emissions were phenanthrene/anthracene (21 percent), unidentified POMs (17 percent), benz(a)anthracene/chrysene (11 percent), C_1-phenanthrenes/anthracenes (10 percent), pyrenes (8 percent), fluoranthene (6 percent), high molecular weight POMs (6 percent), and benz(a)fluorene (6 percent).

[p] The primary constituents of total POM emissions were phenanthrene/anthracene (27 percent), benz(a)anthracene/chrysene (16 percent), pyrenes (16 percent), unidentified POMs (15 percent), and high molecular weight POMs (15 percent).

[q] Factor represents both particulate and gaseous POM emissions.

TABLE 15. POM EMISSION FACTORS FOR WOOD-FIRED RESIDENTIAL HEATING SOURCES (Continued)

---

[r] The primary constituents of total POM emissions were anthracene/phenanthrene (33 percent) and methyl anthracenes/phenanthrenes (11 percent). Remaining POM emissions consisted of ten POM compounds each constituting an unquantifiable portion of the total.

[s] The primary constituents of total POM emissions were anthracene/phenanthrene (31 percent), C_2-alkyl-benzanthracenes/benzophenanthrenes/chrysenes (25 percent), methyl anthracenes/phenanthrenes (9 percent), fluoranthene (7 percent), pyrene (7 percent), methyl fluoranthenes/pyrenes (6 percent), benzofluoranthenes (6 percent), and benz(a)anthracene/chrysene (5 percent).

[t] The primary constituents of total POM emissions were methyl anthracenes/phenanthrenes (23 percent), anthracene/phenanthrene (19 percent), fluoranthene (4 percent), pyrene (4 percent), methyl fluoranthenes/pyrenes (4 percent), methyl benzanthracenes/benzphenanthrenes/chrysenes (4 percent), benzofluoranthenes (4 percent), benzo(g,h,i)perylene (4 percent), benzopyrenes/perylene (4 percent), C_2-alkyl anthracenes/phenanthrenes (4 percent), and benz(a)anthracene/chrysene (4 percent).

[u] The primary constituents of total POM emissions were anthracene/phenanthrene (35 percent), methyl anthracenes/phenanthrenes (10 percent), fluoranthene (8 percent), pyrene (7 percent), benzofluoranthenes (6 percent), methyl fluoranthenes/pyrenes (6 percent), and benz(a)anthracene/chrysene (6 percent).

[v] The primary constituents of total POM emissions were anthracene/phenanthrene (39 percent), methyl anthracenes/phenanthrenes (14 percent), fluoranthene (9 percent), pyrene (6 percent), methyl fluoranthenes/pyrenes (4 percent), benzofluoranthenes (4 percent), and benz(a)anthracene/chrysene (4 percent).

[w] The primary constituents of total POM emissions were anthracene/phenanthrene (33 percent), fluoranthene (11 percent), pyrene (9 percent), methyl anthracenes/phenanthrenes (9 percent), benzofluoranthenes (6 percent), methyl fluoranthenes/pyrenes (5 percent), and benzopyrenes/perylene (4 percent).

[x] The primary constituents of total POM emissions were anthracene/phenanthrene (32 percent), methyl anthracenes/phenanthrenes (16 percent), benz(a)-anthracene/chrysene, (12 percent), fluoranthene (6 percent), pyrene (6 percent), methyl fluoranthenes/pyrenes (4 percent), benzofluoranthenes (4 percent), and cyclopenta(c,d)pyrene (4 percent).

[y] The primary constituents of total POM emissions were anthracene/phenanthrene (39 percent), methyl anthracenes/phenanthrenes (11 percent), methyl fluoranthenes/pyrenes (6 percent), benzofluoranthenes (6 percent), pyrene (5 percent), benz(a)anthracene/chrysene (5 percent), and fluoranthene (5 percent).

[z] Factor represents only particulate POM emissions.

TABLE 15. POM EMISSION FACTORS FOR WOOD-FIRED RESIDENTIAL HEATING SOURCES (Continued)

[aa] Practically no POM compounds were measured in the gaseous phase. Factor shown represents primarily particulate POM emissions.

[bb] Factor represents the average POM emissions for 15 source tests conducted over the full range of wood loads and damper settings. Specific POM compounds identified were naphthalene/methyl naphthalenes/phenylnaphthalenes, acenaphthylene, acenaphthene, fluorene, phenanthrene/anthracene, fluoranthene, pyrene, benzo(g,h,i)fluoranthene, chrysene/benzo(a)anthracene, benzo(b)fluoranthene/benz/fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene/benzo(g,h,i)perylene, and dibenzo(a,h)anthracene. The primary constituents of total POM emissions were naphthalene/methyl naphthalenes/phenylnaphthalenes (49 percent), phenanthrene/anthracene (16 percent), acenaphthylene (10 percent), and chrysene/benzo(a)anthracene (4 percent). All POM compounds measured were in the gaseous phase except for one test where particulate POM compounds were detected.

[cc] Factor represents the average POM emissions for six source tests conducted over the full range of wood loads and damper settings. All of the POM compounds listed in footnote bb were detected in these tests except for acenaphthene and dibenzo(a,h)anthracene. The primary constituents of total POM emissions were naphthalene/methyl naphthalenes/phenylnaphthalenes (48 percent), phenanthrene/anthracene (22 percent), acenaphthylene (9 percent), fluorene (4 percent), fluoranthene (4 percent), and pyrene (4 percent). All POM emissions were found to be in the gaseous phase.

[dd] Factor represents the average POM emissions for six source tests conducted over the full range of wood loads and damper settings. All of the POM compounds listed in footnote bb were also detected in these tests. The primary constituents of total POM emissions were naphthalene/methyl naphthalenes/phenylnaphthalenes (51 percent), phenanthrene/anthracene (18 percent), acenaphthylene (7 percent), acenaphthene (4 percent), and chrysene/benzo(a)anthracene (4 percent). All POM emissions were found to be in the gaseous phase.

[ee] Factor represents the average POM emissions for two source tests conducted at high and low wood loads at a 30 percent damper setting. All of the POM compounds listed in footnote bb were detected in these tests except for dibenzo(a,h)anthracene. The primary constituents of total POM emissions were naphthalene/methyl naphthalenes/phenylnaphthalenes (53 percent), phenanthrene/anthracene (18 percent), acenaphthylene (9 percent), acenaphthene (3 percent), and fluoranthene (3 percent). All POM emissions were found to be in the gaseous phase.

[ff] Factor represents the average POM emissions for two source tests conducted at high and low wood loads at a 30 percent damper setting. All of the POM compounds listed in footnote bb were detected in these tests except for indeno(1,2,3-c,d)pyrene/benzo(g,h,i)perylene and dibenzo(a,h)anthracene. The primary constituents of total POM emissions were naphthalene/methyl naphthalenes/phenylnaphthalenes (54 percent), phenanthrene/anthracene (19 percent), acenaphthylene (10 percent), acenaphthene (3 percent), and fluoranthene (3 percent). All POM emissions were found to be in the gaseous phase.

0.023 mg/kg (average of 0.019 mg/kg). Total particulate and gaseous POM emissions have been measured to range from 24.9 to 36.5 mg/kg, with an average factor being 32.5 mg/kg. Although not directly comparable, the two sets of results do reaffirm the probable importance of gaseous POM emissions from wood combustion sources. Anthracene, phenanthrene, fluoranthene, and methyl anthracenes/phenanthrenes constituted the bulk of the POM emissions measured from fireplaces.[29-33]

A more discrete analysis of total POM emissions from wood-fired residential heaters is provided in Table 16. Total POM emission factors under various burn rate conditions are presented for an oak fuel and a fir fuel test. For the oak fuel test, it appears that total POM emissions are generally greatest under low burn rate conditions and less under high burn conditions. This behavior is consistent with the general theory of POM formation in combustion systems.[36]

For the fir fuel test, somewhat different results occurred which indicate highest POM emissions during the medium burn rate period and the lowest emissions during the low burn rate period. No data were presented in the emission test report to explain the change in the emission pattern when the fir fuel was used.[36]

Natural Gas Combustion--

As shown in Table 17, POM emission factors are predominantly only available for total particulate POM emissions from natural gas combustion. Uncontrolled total particulate POM emissions from natural gas combustion sources ranged from 0.28 to 27.5 pg/J (0.65 to 63.8 lb/10^{12} Btu), with the average factor being 11.2 pg/J (26.0 lb/10^{12} Btu). Pyrene, fluoranthene, coronene, and benzo(g,h,i)perylene accounted for the majority of total particulate POM measured from natural gas combustion.[12]

TABLE 16. POM EMISSION FACTORS FOR UNCONTROLLED WOOD-FIRED HEATERS UNDER VARIOUS BURN CONDITIONS[36]

Red Oak Fuel	Total POM Emission Factor, g/kg[a] (lb/10^6 Btu)[b]		
Heater Test	Low Burn[c]	High Burn[c]	Low/High Burn Mean[c]
1	0.31 (0.065)	0.003 (0.0006)	0.16 (0.033)
2	0.023 (0.006)	0.008 (0.0017)	0.016 (0.0038)
3	0.11 (0.027)	0.006 (0.0013)	0.056 (0.014)
4	0.24 (0.046)	0.20 (0.042)	0.22 (0.044)
5	0.005 (0.0010)	0.050 (0.012)	0.027 (0.0062)
Mean of All Tests	0.14 (0.029)	0.053 (0.012)	0.095 (0.020)

Fir Brand Fuel	Total POM Emission Factor, g/kg[a] (lb/10^6 Btu)[b]			
Heater Test	Low Burn[c]	Medium Burn[c]	High Burn[c]	Low/Med/High Burn Mean[c]
1	0.13 (0.026)	---	0.25 (0.057)	0.19 (0.042)
2	0.27 (0.051)	0.86 (0.19)	0.26 (0.059)	0.46 (0.10)
3	0.021 (0.004)	---	0.29 (0.070)	0.16 (0.037)
Mean of All Tests	0.14 (0.027)	0.86 (0.19)	0.26 (0.062)	0.30 (0.065)

[a] Factor expressed in terms of grams of emissions per kilogram of wood burned.

[b] Factor expressed in terms of pounds of emissions per million Btus of heat input.

[c] Factors represent both particulate and gaseous POM emissions.

TABLE 17. UNCONTROLLED POM EMISSION FACTORS FOR NATURAL GAS-FIRED SOURCES

Boiler Type	Application	Total POM Emission Factor pg/J-Heat Input ($lb/10^{12}$ Btu-heat Input)	Reference
Firetube	Process heating	0.28 (0.65)[a,b]	12
Scotch marine	Hospital heating	27.4 (63.5)[a,c]	12
Double shell	Home heating	0.48 (1.1)[a,d]	12
Hot air furnace	Home heating	0.33 (0.77)[a,e]	12
Wall space heater	Home heating	27.5 (63.8)[a,f]	12
Data not available	Process heating	14.3 (33.2)[g]	16

[a] Factors represent primarily particulate POM compounds. Ten specific POM compounds were analyzed for during these tests.

[b] Specific compounds identified were benzo(a)pyrene, pyrene, coronene, and fluoranthene. Pyrene and fluoranthene constituted 88 percent of total POM emissions.

[c] Specific compounds identified were benzo(a)pyrene, benzo(e)pyrene, benzo(g,h,i)perylene, pyrene, coronene, anthanthrene, and fluoranthene. The primary constituents of total POM emissions were pyrene (62 percent), coronene (18 percent), fluoranthene (10 percent), and benzo(g,h,i)perylene (6 percent).

[d] Specific compounds identified were benzo(a)pyrene, pyrene, and fluoranthene. Fluoranthene accounted for 63 percent of total POM emissions, pyrene 33 percent, and benzo(a)pyrene 4 percent.

[e] Specific compounds identified were benzo(a)pyrene, benzo(e)pyrene, pyrene, phenanthrene, and fluoranthene. Pyrene, fluoranthene, and phenanthrene accounted for 89 percent of total POM emissions.

[f] Specific compounds identified were benzo(a)pyrene, benzo(e)pyrene, benzo(g,h,i)perylene, pyrene, coronene, anthanthrene, and fluoranthene. The primary constituents of total POM emissions were pyrene (55 percent), fluoranthene (28 percent), benzo(g,h,i)perylene (8 percent), and benzo(e)pyrene (5 percent).

[g] Factor represents both particulate and gaseous POM emissions. Specific compounds identified were naphthalene, biphenyl, phenanthrene, 2-methylphenanthrene, fluoranthene, and pyrene. Naphthalene accounted for 44 percent of total POM emissions, fluoranthene 25 percent, and biphenyl 23 percent.

One POM emission factor of 14.3 pg/J (33.2 lb/10^{12} Btu) was identified for total particulate and gaseous POM emissions from natural gas combustion. The major POM components of this factor were naphthalene, fluoranthene, and biphenyl.[16]

Bagasse Combustion--

Polycyclic organic matter emission factors for bagasse combustion are very limited as indicated in Table 18. Total particulate and gaseous POM emissions from multicyclone-controlled bagasse boilers have been found to range from 17.2 to 77.5 pg/J (40 to 180 lb/10^{12} Btu), with the average emission rate being 54.5 pg/J (127 lb/10^{12} Btu). The predominant POM compounds that have been measured in bagasse boiler emissions are 3-methylcholanthrene and 7,12-dimethylbenz(a)anthracene.[37] In coal, oil, and natural gas combustion, emissions of these POM compounds either were not found or were only present in trace amounts. Although data are limited, it appears in general that POM emissions from bagasse combustion are, on a unit basis, more significant than those from other fuel combustion sources with the exception of wood-fired combustion sources. One possible reason for these higher emissions is the relatively high moisture content of bagasse. A high fuel moisture content causes lower combustion temperatures, less efficient combustion, and more smoldering which in turn promotes POM formation.

Waste Oil Combustion--

Polycyclic organic matter emissions from waste oil combustion in space heaters have been measured and reported in the literature.[38] Waste automotive crankcase oil was burned in a vaporizing pot burner type space heater and an air atomizing burner type space heater. Emissions were analyzed to identify and quantify the amounts of 18 different POM compounds possibly present. Total particulate and gaseous POM emissions from the vaporizing pot type heater ranged from 13.3 ug/l (50.2 ug/gal) to 25.1 ug/l (94.4 ug/gal), with the average being 19.2 ug/l (72.3 ug/gal). The

TABLE 18. POM EMISSION FACTORS FOR BAGASSE-FIRED INDUSTRIAL BOILERS[37]

Source	Total POM Emission Factors	
	kg/Mg (lb/ton)[a]	pg/J (lb/10^{12} Btu)[b]
Bagasse Boiler A[c,d]	0.00085 (0.0016)[e]	77.5 (180)[e]
Bagasse Boiler B[c,g]	0.00015 - 0.00074[f] (0.00035 - 0.0014)[f]	17.2 - 68.9[f] (40 - 160)[f]

[a] Units are expressed in terms of mass total POM emitted per mass of bagasse burned.

[b] Units are expressed in terms of mass total POM emitted per unit of heat input to the boiler.

[c] Eight specific POM compounds were analyzed for in these tests.

[d] Source A represents the emissions of two bagasse-fired boilers each controlled by a multicyclone and vented to one common exhaust stack.

[e] Emissions consist of 3-methylcholanthrene and an unknown POM compound. Results represent particulate and gaseous POM emissions.

[f] Emissions consist of 7,12-dimethylbenz(a)anthracene, 3-methylcholanthrene, and two unknown POM compounds. Results represent particulate and gaseous POM emissions.

[g] Source B represents the emissions of a single bagasse-fired boiler controlled by a multicyclone.

predominant POM compounds measured in the waste oil combustion emissions were phenanthrene, naphthalene, benzo(a)pyrene, benzo(e)pyrene, perylene, and benzofluoranthenes.[38]

Total particulate and gaseous POM emissions from the air atomizing type heater ranged from 1.3 ug/l (6.0 ug/gal) to 2.2 ug/l (10.1 ug/gal). As with the vaporizing pot heater, phenanthrene was the predominant POM compound measured in emissions from the air atomizing type heater. Naphthalene, fluorene, pyrene, perylene, fluoranthene, and indeno(1,2,3-c,d)pyrene were also relatively major constituents of total POM emissions.[38]

If a heating value for waste oil of 115,875 Btu/gal is assumed,[39] POM emissions from the vaporizing pot type space heater can be shown to be comparable to several of the POM emission factors for residual oil combustion in Table 10 and greater than several of the factors for POM emissions from distillate oil in Table 11. Using the 115,875 Btu/gal figure, total POM emissions from the vaporizing pot type heater would range from 0.41 to 0.77 pg/J (0.95 to 1.8 lb/10^{12} Btu), with the average emission factor being 0.59 pg/J (1.4 lb/10^{12} Btu).[38] Total POM emissions from the air atomizing type heater would be only 0.049 to 0.083 pg/J (0.11 to 0.19 lb/10^{12} Btu), and therefore do not appear to be comparable to POM emissions from either residual or distillate oil combustion.

Source Locations

The sheer numbers of individual sources within each of the major stationary combustion sectors (utility, industrial, commercial, residential) prohibit site specific listings in this document. However, location trends and contact groups for individual source identification can be presented. In the utility sector, coal-fired sources are concentrated in the States of Ohio, Indiana, West Virginia, Pennsylvania, and Illinois. Other States with substantial coal-fired capacity are Texas, Georgia, Kentucky, Michigan, Missouri, North Carolina, Alabama, and Tennessee.[6,40]

Residual oil-fired utility boilers are located primarily in New York, Florida, Massachusetts, Connecticut, and California. In 19 States, little or no residual oil is burned for utility boiler purposes. The majority of natural gas burned for utility purposes occurs in Texas, California, and Louisiana. Other States with significant utility sector natural gas combustion include Florida, New York, New Jersey, and Mississippi.[6,40]

Information on precise utility plant locations can be obtained by contacting utility industry trade associations like the Electric Power Research Institute (EPRI) in Palo Alto, California (415-855-2000); the Edison Electric Institute (EEI) in Washington, D.C. (202-828-7400); or the Energy Information Administration (EIA) of the U. S. Department of Energy (DOE) in Washington, D.C. Publications by EIA/DOE on the utility industry such as, Inventory of Power Plants in the United States - 1984,[11] [DOE/EIA-0095(84), July 1985] also would be useful in determining specific facility locations, sizes, and fuel use.

Industrial fuel combustion sources are located throughout the United States, but tend to follow industry and population location trends. Most of the coal-fired industrial boiler sources are located in the Great Lakes, Great Plains, Appalachian, and Southeast regions. Oil-fired boilers are common in the New England, Southeast, and Upper Atlantic regions, while the highest concentration of natural gas-fired units is found in the Gulf Coast and Pacific Southwest regions.[6,40] Wood-fired boilers tend to be located almost exclusively at pulp and paper, lumber products and furniture industry facilities. These industries are concentrated in the Southeast, Gulf Coast, Appalachian, and Pacific Northwest regions.[6] Trade associations such as the American Boiler Manufacturers Association (ABMA) in Arlington, Virginia (703-522-7350) and the Council of Industrial Boiler Owners (CIBO) in Fairfax Station, Virginia (703-250-9042) would also be good groups to contact regarding industrial boiler locations and trends.

Commercial fuel combustion sources are generally tied directly to population locations. The size of a commercial unit will probably dictate the ease with which it can be located. Larger units may be on a par with some industrial sources and ABMA or CIBO may be a source of information. State air agency permits may also be good sources of information on locations and characteristics of commercial combustion units, except that most States have cut-offs for reporting and permitting of boilers and many commercial units fall below the cut-off.

Fuel use patterns for commercial boilers are likely to parallel those described above for industrial boilers, since fuel choice decisions in both categories are made on the basis of fuel availability and prices (including transportation costs). The greatest coal consumption for commercial combustion occurs in Pennsylvania, Ohio, Indiana, and Kentucky. Commercial fuel oil consumption is greatest in the States of New York, Louisiana, California, and New Jersey. For commercial combustion purposes, California, Illinois, Texas, and Michigan consume the largest amounts of natural gas.[6,40]

Locations of residential combustion sources are also tied directly to population trends with the exception of wood-fired sources. Wood-fired residential units are generally concentrated in heavily forested areas of the United States, which again reflects fuel selection based on availability and price. Coal consumption for residential combustion purposes occurs mainly in Pennsylvania, Ohio, New York, and Indiana. Residential oil consumption is greatest in New York, New Jersey, Massachusetts, and Pennsylvania. California, Illinois, Ohio, and Michigan have the largest natural gas consumption for residential combustion purposes.

MOBILE SOURCES OF POM

Process Description

The internal combustion engines of mobile sources emit gas-phase hydrocarbons and particulate organic material as products of incomplete combustion and as noncombusted (leaked) fuel, fuel additives, and lubricants. Some POM, such as the nitro derivatives, are formed after the exhaust is released to the atmosphere. Nitro-PAH is formed when PAH in the particulate reacts with nitrogen oxides in the exhaust.[41] Temperatures in the combustion chamber and exhaust system and volume flow rates influence POM formation and emission rate. These factors are, in turn, affected by engine size, design, working load, and operating speed.

Gasoline engine combustion occurs at temperatures around 3500°C (6332°F) at near-stoichiometric oxygen levels. Exhaust from gasoline engines is generally at temperatures between 400 and 600°C (752 to 1112°F). Diesel engines operate at combustion temperatures of about 2000°C with an excess of oxygen. Diesel exhaust temperatures range from 200 to 400°C (392 to 752°F).[42]

After exhaust is released from a vehicle, it is diluted approximately 1000-fold in the first few seconds and cools very rapidly.[42] Polycyclic organic matter and other vapor-phase organic chemicals often condense on carbon nuclei and other particles in the exhaust that are also products of incomplete combustion. Polycyclic organic matter emissions from gasoline engine vehicles with oxidation catalysts are generally sulfuric acid droplets less than 0.1 um in diameter that have organic compounds adsorbed on their surfaces.[42] Particulate emissions from diesels are predominately elemental carbon particles that form chains or clusters approximately 0.15 um in diameter onto which the organic compounds are adsorbed.[42]

The heavier POMs, such as benzo(a)pyrene, are found predominantly on particles less than 1 um in diameter, while the lighter POMs are mostly in the vapor phase.[45] Since the majority of POMs with the greatest mutagenicity are the heavier POMs, particulate POM emissions from mobile sources have generally been of the most interest.

Engine oil accumulates PAHs and may emit them when the oil leaks into the combustion chamber or the exhaust system and survives the emission process. Peake and Parker[43] estimated that crankcase oil accumulates up to ten times as much POM per mile traveled as is emitted in the exhaust.

Handa et al.[44] calculated that between 28 and 36 percent of the benzo(a)pyrene, benzo(a)anthracene, chrysene, and pyrene in engine oil that leaks into an automobile's combustion chamber or exhaust system is emitted.

Two-cycle, or two-stroke, engines are internal combustion engines that do not have oil crankcases. They operate on a mixture of oil and gas, with the oil being the sole source of lubrication in the system. Motorcycles, outboard motors, lawnmowers, and chain saws are examples of equipment that typically use two-cycle engines.

The contributions of various types of mobile sources to total mobile source PAH (the major subset of POM) and 1-nitropyrene emissions in 1979 are shown in Table 19. Most of the PAH emissions from mobile sources in 1979 originated from older gasoline automobiles not equipped with catalytic converters.[42] However, emissions from this category are declining as older gasoline automobiles are taken out of service. The use of diesel fuel is increasing,[42,46] so emissions from diesel vehicles are expected to increase.

Factors Influencing POM Emissions

Gasoline-Fueled Vehicles--

Emissions of POM from gasoline automobiles and trucks are influenced by a number of factors. These include vehicle effects, such as:

- air-to-fuel ratio,
- presence of emission controls,
- mode of operation, and
- extent of deterioration; and

fuel effects, such as:

- aromaticity,
- POM content, and
- the presence of additives or lubricants.

TABLE 19. CONTRIBUTIONS OF VARIOUS MOBILE SOURCE CATEGORIES TO TOTAL MOBILE SOURCE PAH AND 1-NITROPYRENE EMISSIONS IN 1979[42]

Category	PAH Emission, %		1-Nitropyrene Emission, %	
Motor Vehicles:				
Passenger cars:				
Noncatalyst	29.1		0.9	
Oxidation catalyst	3.8		0.6	
Diesel	0.6		1.3	
Trucks, <33,000 lb:				
Spark-ignition	14.7		0.5	
Diesel	0.6		1.2	
Trucks, >33,000 lb.				
Spark-ignition	0.7		0.02	
Diesel	11.8		25.1	
Buses:				
Spark-ignition	0.3		0.01	
Diesel	0.6		1.0	
Motorcycles	0.3	62.5	0.01	30.6
Other Mobile Sources:				
Railroads	3.3		6.9	
Ships	7.1		13.7	
Aircraft	16.8		34.7	
Farm	4.0		6.8	
Military	0.6		1.3	
Miscellaneous	6.0	37.8	5.6	69.0
		100.3		99.6

Air-to-fuel ratios less than stoichiometric promote incomplete combustion and therefore increase emissions of carbon monoxide and POM. It has been estimated that 30 times more benzo(a)pyrene is produced at an air-to-fuel ratio of 10:1 than at 14:1.[47]

Modifications to vehicles since 1967 reduced benzo(a)pyrene emissions by 85 percent by the early 1970s.[42] Table 20 shows benzo(a)pyrene emission factors measured for automobiles produced between 1958 and the early 1970s and having different levels of emission control.

The effect of vehicle operation mode is related to the air-to-fuel ratio. Cold-start operation will cause higher POM emissions because the engine is operating in a choked, or fuel-rich, condition. Higher engine load also may increase POM emissions during cold starts. The temperature of the engine coolant, however, was not found to affect POM emissions.[45] Hangebrauck et al.[48] measured benzo(a)pyrene emissions from a 6-cylinder dynamometer-mounted engine at various modes of operation. They found that the highest benzo(a)pyrene emission rate occurred during acceleration.

The extent of deterioration, or the mileage, of a vehicle has been shown to affect POM emission rates significantly. Increasing deterioration over a threshold level causes increased emission rates. Hangebrauck et al.[48] found that benzo(a)pyrene emission rates of both 6-cylinder and V-8 automobiles increased sharply at 50,000 miles. While the overall benzo(a)pyrene emission rate was 28 ug/mile, the average emission rate for the newer, lower-mileage automobiles was 5.5 ug/mile. Table 21 shows benzo(a)pyrene emission rates estimated by several researchers that suggest that emissions increase with vehicle mileage. All the emission rates in Table 21 were measured by sampling particulate emissions from a V-8 gasoline engine mounted on a dynamometer and operated to simulate city driving. More recently, Handa et al.[49] estimated that average POM emission rates increase linearly with mileage above 12,000 miles.

TABLE 20. BENZO(A)PYRENE EMISSION FACTORS AT VARIOUS LEVELS OF EMISSION CONTROL[47]

Level of Control	Benzo(a)pyrene Emission Factors (ug/gal of fuel consumed)
Uncontrolled (1956 - 1964)	170
Uncontrolled (1966)	45 - 70
Vehicle modification (1968)	20 - 30
Thermal reactors and catalytic converters (early 1970s)	≤10

TABLE 21. BENZO(A)PYRENE EMISSION RATES AT VARIOUS MILEAGE INTERVALS[48]

Mileage Interval	BaP Emission Rate (ug/mile)[a]
8,000 - 12,000	25[b]
19,300 - 25,500	16
25,500 - 29,000	24
29,000 - 33,000	74[c]

[a] ug/mile calculated from emissions measured in ug/min based on 23 mph average cycle speed.

[b] Includes high BaP content of condenser-collected tar.

[c] Malfunction of engine was reported for this emission rate.

Increased oil consumption is a primary cause of the increased POM emissions with mileage. Hoffman et al.[50] observed about a 12-fold increase in benzo(a)pyrene emissions when oil consumption increased from 1 quart per 1600 miles to 1 quart per 200 miles. The higher quantities of oil in older, more worn cylinders provides more intermediates for POM formation, and POM becomes concentrated in the oil.[42]

Another cause of increased POM emissions with mileage is the formation of deposits in the combustion chamber. Total hydrocarbon emissions increase with mileage until the deposits become stabilized at several thousand miles.[42] Gross[51] found that gasoline vehicles with unstabilized deposits emit five to six times more benzo(a)pyrene when fuel containing high levels of polynuclear aromatics (PNA) is used than when low-PNA fuel is used. Vehicles with stabilized deposits emit two to three times more benzo(a)pyrene with the high-PNA fuels. Table 22 summarizes the results of this study.

Several early studies suggested that POM emissions increased with increasing aromatic content of fuel.[52-54] Most of these studies used experimental fuel mixtures rather than commercially available fuels. Gross'[55] data show that POM emissions did not increase at higher fuel aromaticity in unleaded gasoline vehicles with stabilized deposits. The nature of the combustion chamber deposits may offset the increase in POM emissions that may be caused by high fuel aromaticity. However, Hoffman et al.[56] found no such relationship. Gross[55] observed progressive stabilization of the deposits, a subsequent gradual decline in POM emissions, and the possible carry-over of POM from a high-POM fuel in one test to emissions in the following test. His observations indicate that a process of deposition and subsequent emission may be the way in which fuel POM is emitted.[55]

Diesel-Fueled Vehicles--

Polycyclic organic matter emissions from diesel-fueled vehicles are increased by overloading and poor engine maintenance.[47] However, even under normal operating conditions, diesel vehicles emit more POM than gasoline

TABLE 22. CHANGE IN AVERAGE POM EMISSIONS WITH DEPOSIT CONDITION AND POM CONTENT OF FUELS[51]

Deposit Condition	Average Ratio of Emissions with High/Low POM Fuels[a]	
	Benzo(a)pyrene	Benzo(a)anthracene
Unstabilized	5.6	7.0
Stabilized	2.4	2.1

[a] POM emissions averaged for a variety of emission test fuels and three automobiles: 1966 Plymouth, 1968 Chevrolet, and 1970 Chevrolet.

vehicles. This may be due, in part, to the lower combustion chamber temperatures typical of diesel engines.[47] Diesel automobiles emit 30 to 100 times more particulate matter per mile than gasoline automobiles equipped with catalytic converters.[47] Engine oil is probably not a significant source of POM in diesel exhaust because diesel combustion chambers do not operate under vacuum and, therefore, oil is less likely to be drawn into the chamber.[57]

Fuel POM content appears to be insignificant in determining the rate of POM emission from diesel engines. Twenty different diesel fuels, ranging widely in POM content, were found to differ very little in the rate of POM emissions associated with them.[58] The diesel fuels contained lower POM concentrations [1 to 420 ppb benzo(a)pyrene] than gasoline [up to 3100 ppb benzo(a)pyrene].[58]

Over 50 nitro-PAH compounds (a subset of POM) have been found in diesel particulate emissions.[42] 1-Nitropyrene is by far the most abundant nitro-PAH in diesel exhaust. Gasoline automobiles have been found to emit only two nitro-PAH: 1-nitropyrene and 1-nitrochrysene.[49]

Two-Cycle Engines--

A study on emissions of a two-cycle motorcycle engine suggests that benzo(a)pyrene emissions are directly related to the oil concentration in the gasoline/oil fuel mixture.[47] However, Levin et al.[59] attributed POM in two-cycle engine exhaust predominantly to unburned gasoline released by the engine. The oil in the fuel was not considered important. This conclusion was determined by using chromatography to analyze the gasoline fuel with and without two-cycle oil. The chromatographs showed no significant change in POM content with the oil addition. Consequently, since the chromatographs of the emission samples and the gasoline were so similar, it was theorized that the gasoline was the source of the POM.

Aircraft--

Very limited information is available in the literature on POM emissions from aircraft. However, the data that are available suggest the following.[60]

1. Emissions of POM from aircraft turbine engines increase at lower power settings.
2. Emissions of POM from aircraft increase with decreases in fuel sulfur content.

Rubber Tire Wear--

Carbon black and other tire materials that may contain POM are released to the atmosphere through normal tire wear.[47] Tire burning for disposal may be a larger source of POM.[47]

Emission Factors

Gasoline Vehicles--

Automobiles--The U. S. EPA estimated emission factors for benzo(a)pyrene using data from Gross.[55,61] Minimum, maximum, and intermediate emission factors were developed for particulate emissions sampled by filtration during cold-start cycles.[62] These emission factors are shown in Table 23.

The Committee on Pyrene and Selected Analogues summarized what it called the best current measurements of POM emissions from mobile sources. Committee members compiled emission rates (ug/gal of fuel) for numerous POMs and their derivatives from nine studies conducted between 1977 and 1981.[42] The Committee also derived emission factors from the existing factors for vehicle categories for which no data were available. The measured and

TABLE 23. ESTIMATED PARTICULATE BENZO(A)PYRENE EMISSION FACTORS FOR GASOLINE AUTOMOBILES, MODEL YEARS 1966-1976[61]

Model Year	Fuel Type	Control	Emission Factor (ug/gal)		
			Minimum	Maximum	Intermediate[a]
1966	Leaded	None	130	330	170[c]
1966	Unleaded	None	76	460	160
1966	Unleaded	Engine modification	8.7	180	29
1968	Leaded	Engine modification	---	---	36[b]
1968	Leaded	RAM thermal reactor	---	---	1.6[b]
1970	Leaded	Engine modification	8.0	28	28[b]
1970	Unleaded	Engine modification	12	72	14
1970	Unleaded	Monel/PTX-5 catalyst	---	---	1.1[b]
1976	Weighted by 1976 auto population	---	21	49	34

[a] Geometric means, unless noted otherwise.

[b] Best estimates of emissions for the same series of tests and using the same fuels.

derived factors are shown in Table 24. The derived emission factors have an uncertainty of a factor of two or more[42] and are generally overestimates compared to values reported in the literature.

More recently, Handa et al. estimated particulate PAH and nitro-PAH emission rates for diesel and gasoline motor vehicles from traffic densities and atmospheric levels of the particulates in two tunnels in Japan.[49] Average emission rates (ug/h) estimated in the Nihonzaka and Tsuburano tunnels were averaged and divided by the average vehicle speed in the tunnel (80 km/hour, or approximately 50 mi/hour) to calculate emission rates in ug/mi. These emission rates are shown in Table 25. The emission rates of the six PAHs measured were higher for gasoline automobiles than for diesels, whereas nitro-PAH emission rates were higher for diesels.

Lang et al. measured total particulate and dichloromethane (DCM) - soluble organic fraction (SOF) emission rates from gasoline automobiles using two sequential test procedures: the cold start Federal Test Procedure (FTP) followed by the repetitive hot start Highway Fuel Economy Test (HWFET).[63] Benzo(a)pyrene, pyrene, and nitropyrene were analyzed from the organics. Particulates were sampled by a dilution-filtrate method. The authors indicated that because the filtrate procedure was used, the POM emission rates may not indicate total exhaust emissions, but they are a relative measure of the compounds assayed for mutagenicity in the same study. Considerable uncertainty is associated with the pyrene emission rates. The conventional filtration procedures used do not allow quantitative measurements of pyrene because pyrene is distributed between the gaseous and particulate phases.[64,65] In addition, DCM is not the best solvent for extracting POM from particulate matter.[63] The results of the two emission tests for leaded and unleaded gasoline vehicles are shown in Table 26.

All particulate organic emissions except nitro-pyrene were higher from leaded than from unleaded gasoline vehicles. Total particulate organic emission rates from leaded gasoline vehicles were 2.7 times higher under

TABLE 24. MEASURED AND DERIVED POM EMISSION FACTORS FOR MOBILE SOURCES[42]

POM Compound	Emission Rate (ug/gal)[a]					
	Gasoline				Diesel	Motorcycles
	Light-Duty			Heavy-Duty		
	Noncatalyst Leaded Fuel[b]	Oxidation Catalyst, Unleaded Fuel	Three-Way Catalyst, Unleaded Fuel	Noncatalyst, Leaded Fuel	Noncatalyst	Leaded Fuel
Anthracene	2,239	410	48	2,239	2,633	2,239
Phenanthrene	9,084	1,664	196	9,084	10,681	9,084
Methylphenanthrene	5,678	1,040	123	5,678	6,676	1,113
Dimethylfluorene	2,972	544	64	2,972	3,495	2,972
Dimethylphenanthrene	2,014	369	44	2,014	2,368	2,014
Fluoranthene	4,758	871	103	4,758	5,595	4,758
Pyrene	6,031	1,105	130	6,031	7,091	6,031
Benzofluorene	750	137	16	750	882	750
Benzoanthracene	231	42	5	231	272	231
Triphenylene	189	35	4	189	222	189
Cyclopentapyrene	2,472	453	53	2,472	2,907	2,472
Chrysene	939	172	20	939	1,104	939
Indenofluoranthene	83	15	2	83	98	83
Indenopyrene	191	35	4	191	225	191
Methylchrysene	38	7	1	38	45	38
1-Nitropyrene	3.5	4	0.4	4	271	3.5
Benzofluoranthene	699	123	15	669	840	669
Benzo(e)pyrene	325	60	7	325	382	325
Benzo(a)pyrene	273	50	6	273	321	273
Perylene	27	5	1	27	32	27
Cyclopentabenzopyrene	163	30	4	163	192	163
Benzochrysene	4	1	0.1	4	5	4
Anthanthrene	140	26	3	140	165	140
Dibenzanthracene	79	14	2	79	93	79
Benzoperylene	723	132	16	723	850	723
Coronene	502	92	11	502	590	502
Cyclopentabenzopyrelene	114	21	2	114	134	114

[a] All emission factors are derived except those for noncatalyst leaded gasoline vehicles.

[b] Average of measured emissions from References 62, 65, 66, and 67.

TABLE 25. AVERAGE EMISSION RATES OF PARTICULATE POMs FROM GASOLINE AND DIESEL VEHICLES IN TWO TUNNELS IN JAPAN AT AN AVERAGE SPEED OF 50 mi/hr[44]

POM	Gasoline (ug/mi)	Diesel (ug/mi)
Pyrene	109	5.5
Chrysene	9.1	6.4
Benzo(a)anthracene	5.5	5.2
Perylene	0.93	0.52
Benzo(a)pyrene	4.0	2.1
Benzo(g,h,i)perylene	5.6	2.0
1-Nitropyrene	0.028[a]	0.31[b]
1-Nitrochrysene[c]	0.012	0.20

[a] Average of emission rate at low-load conditions (0.013 ug/mi) and high-load conditions (0.044 ug/mi).

[b] Average of emission rate at low-load conditions (0.13 ug/mi) and high-load conditions (0.48 ug/mi).

[c] Emission rate at high-load conditions.

TABLE 26. AVERAGE PARTICULATE POM EMISSION RATES FOR GASOLINE VEHICLES, MODEL YEARS 1970-1981, UNDER FTP AND HWFET TEST CYCLES[63]

	FTP		HWFET	
	Leaded Fuel	Unleaded[a] Fuel	Leaded Fuel	Unleaded[a] Fuel
DCM Soluble Organic Fraction (mg/mi)	21.1 ± 13.6	14.4 ± 38.2	23.5 ± 17.3	11.5 ± 20.3
Benzo(a)pyrene (ug/mi)	14.6 ± 15.7	3.2 ± 5.6	0.90 ± 0.65	0.6 ± 1.8
Pyrene (ug/mi)	18.8 ± 19.7	10.0 ± 23.6	5.9 ± 8.6	1.3 ± 3.5
Nitro-pyrene (ug/mi)	0.20 ± 0.13	0.24 ± 0.41	0.39 ± 0.34	0.16 ± 0.23

[a] Catalyst-equipped vehicles.

HWFET than under FTP conditions. However, catalyst-equipped unleaded gasoline vehicles emitted fewer particulates under HWFET conditions. In addition, emissions varied more between vehicles than between operating mode for a given vehicle.

Benzo(a)pyrene emission rates for gasoline were higher under cold-start FTP conditions than hot-start HWFET conditions and higher for leaded-fuel vehicles than for unleaded fuel vehicles. Nitro-pyrene emission rates, however, were similar for leaded and unleaded gasoline vehicles.[44] Nitro-pyrene emissions from diesel vehicles have been found to be 20 to 30 times higher than those from gasoline vehicles.[69]

Lang et al. also addressed the activity of POM in the exhaust by exposing POM to filtered exhaust.[63] They found that the particulate can react with nitrogen oxides in exhaust to form nitro-PAH compounds. The authors suggest that nitro-PAH formed in this way during particulate sampling may account for a significant portion of the direct mutagenicity of diesel particulate emissions.

Handa et al. performed factor analysis on measured POM emissions from test runs of more than 48,279 km (30,000 miles) on 26 Japanese gasoline automobiles in city service.[44] They found that average POM emission rate is linearly related to average car mileage and is significantly affected by engine oil consumption.

Trucks - Comparisons of Gasoline and Diesel--Dietzmann et al. measured gaseous and particulate POM emissions from gasoline and diesel delivery trucks.[70] They used a chassis version of the transient test cycles developed by the Environmental Protection Agency in 1979 for all measurements to compare emissions of diesel and gasoline trucks in service.[71] They found benzo(a)pyrene emission rates of 1.6 ug/mi for the Caterpillar 3208 diesel truck, 17.7 ug/mi for the International Harvester 345 gasoline truck, and 61.2 ug/mi for the Ford 370 gasoline truck. The authors indicated that these emission rates are comparable to those reported by Williams et al.[72]

Automobiles - Comparisons of Gasoline and Diesel--Gibson measured the emission rates of total particulates, pyrene, nitro-pyrene, benzo(a)pyrene, and nitro-benzo(a)pyrene from gasoline and diesel automobiles.[73] Exhaust samples were collected using a chassis dynamometer and dilution tunnel during the 23-minute hot-start phase of the Federal Test Procedure. Commercial gasoline and No. 2 diesel fuels were used in every case. Concentrations of the POM were determined by high performance liquid chromatography (HPLC) with fluorescence detection.[41] The resulting emission rates are shown in Table 27. The rate of POM emission parallels the rate of overall particulate matter emission, which is higher in diesels. The experimental diesel-trap automobile, however, had 79 percent less particulate, 71 percent less pyrene, 80 percent less benzo(a)pyrene, and 63 percent less 1-nitropyrene emissions per mile than the conventional diesel vehicle.[73]

Diesel Vehicles--

Automobiles--General Motors researchers Gibson et al. measured the concentrations of PAH and their derivatives in particulate samples of diesel automobile exhaust.[41] The nitro-PAH were of particular interest because GC/MS and thin layer chromatography-ultraviolet (TLC-UV) spectroscopic analyses have indicated that these compounds are important in the mutagenicity of diesel particulate matter. These researchers used high-performance liquid chromatography with fluorescence detection for their analyses.

The PAH species found in the particulate samples are shown in Table 28. The average concentrations (ng/mg of particulate) of five of the PAH are shown in Table 29. These results are similar to those of Choudhury and Bush, who found that the major components of diesel exhaust particulates from a Volkswagon Rabbit were low-molecular-weight PAHs.[74]

Trucks--Bricklemyer and Spindt measured particulate benzo(a)pyrene and benzo(a)anthracene in diesel exhaust from a turbocharged Mack engine at no load, half load, and full load.[75] Exhaust particulates were collected by

TABLE 27. EMISSION RATES OF OVERALL PARTICULATE MATTER AND PARTICULATE POMs FOR VARIOUS GASOLINE AND DIESEL AUTOMOBILES UNDER THE FTP TEST CYCLE[73]

Source Type	Particulate (mg/mile)[a]	Pyrene (ug/mile)[a]	1-Nitro-pyrene (ug/mile)[a]	Benzo(a)-pyrene (ug/mile)[a]	6-Nitro-Benzo(a)-pyrene (ug/mile)[a]
Unleaded Auto[b] (no catalyst)	23.3±3.6	13.3±2.4	0.10±0.09	4.17±0.68	0.40±0.22
Catalyst Auto[c]	38.2	1.00	0.046	0.07	0.012
Precatalyst Auto[d] (leaded)	44.5±0.8	6.76±0	0.174±0.063	2.72±0.085	1.46±0.74
Diesel Auto[e] (production)	397±48	24.7±8.4	3.2±1.2	0.87±0.08	<0.15
Diesel-Trap Auto[f]	82.4±1.2	7.2	1.2	0.11	0.01

---

[a] Values represent mean ± standard deviation, when available.

[b] 1980 4.3-liter 8-cylinder automobile with its catalyst removed.

[c] 1981 2.5-liter 4-cylinder catalyst automobile.

[d] 1974 5.7-liter 8-cylinder precatalyst automobile.

[e] 1980 5.7-liter 8-cylinder production model diesel automobile.

[f] 1980 5.7-liter diesel automobile equipped with an experimental tube-type trap coated with ceramic fibers to filter the exhaust. The fuel used in this vehicle was No. 2 diesel containing 3.0 g/gal of copper napthenate additive to promote combustion of particles in the trap.

TABLE 28. POM COMPOUNDS ANALYZED BY HPLC-FLUORESCENCE IN DIESEL AUTOMOBILE EXHAUST PARTICULATES[41]

2-Aminofluorene[a]
3-Aminofluoranthene
1-Aminopyrene
Aminobenz(a)anthracene[a]
6-Aminochrysene[a]
6-Aminobenzo(a)pyrene
Aminobenzo(k)fluoranthene
Phenanthrene
Fluoranthene
Benzo(c)fluorene
Pyrene
Benzo(k)fluoranthene
Perylene
Benzo(a)pyrene

[a] Not detected in this study.

TABLE 29. MEAN AND RANGE OF CONCENTRATIONS OF POMs IN EXHAUST PARTICULATE FROM FOUR DIESEL CARS[41]

POM Compound	Mean (ng/mg particulate)	Range (ng/mg particulate)
Pyrene	57.5	18.6 - 105.0
Benzo(a)pyrene	3.9	1.3 - 7.3
Fluoranthene	125	45.2 - 203.0
1-Nitro-pyrene	8.2	6.4 - 9.8
6-Nitro-benzo(a)pyrene	0.88	<0.1 - 1.8

dilution sampling followed by the injection of ^{14}Carbon radioactive tracers and filtration. The POMs were analyzed by ultraviolet spectrophotometry. The POM emission rates in ug/kg of fuel and ug/m^3 of exhaust are shown in Table 30.

Polycyclic organic matter emissions from a test truck powered by a prototype stratified-charge engine, equipped with a catalytic converter, were measured by Lee et al.[76] The exhaust was sampled under steady-speed (30 mph) conditions with a dilution tube and filter-plus-absorbent collection system. The authors suggested that, because the sampling method used had questionable applicability to real-world conditions, the POM emission factors should be used as relative, rather than absolute, measures of emissions. Both filter and gas trap samples were analyzed using solvent extraction and a POM-enrichment step, followed by HPLC and GC/MS analysis. The results of the HPLC and GC/MS techniques agreed within ±10 to 50 percent. The results of the HPLC data are presented in Table 31. They indicate that POM emissions were reduced by 25 to 94 percent by the use of an oxidation catalytic converter. Benzo(a)pyrene was reduced by 78 percent.

Du et al. collected particulates smaller than 1.2 um in diameter in the combustion chamber of an operating diesel engine.[77] They found that, while the concentrations of POMs such as pyrene, benzo(a)pyrene, benz(k)fluoranthene, and fluoranthene were much higher in the combustion chamber than in the exhaust, the concentration of the nitro-PAH 1-nitropyrene was four times higher in the exhaust. The authors concluded that particulate matter is significantly oxidized between the cylinder and the exhaust manifold. Benzo(a)pyrene was measured at a concentration of 92 ug/m^3 in the combustion chamber and estimated at 1.8 ug/m^3 in the exhaust.

Two-Cycle Engines--

Polycyclic organic matter emissions have been qualitatively and quantitatively identified in the exhausts of two-cycle engines. In one study, emissions of a two-cycle motorcycle engine were tested and found to

TABLE 30. PARTICULATE POM EMISSION RATES FROM A TURBOCHARGED MACK ENGINE AT VARIOUS ENGINE LOADS[75]

	ug/kg of Fuel[a]		ug/m^3 of Exhaust[a]	
	Benzo(a)-pyrene	Benzo(a)-anthracene	Benzo(a)-pyrene	Benzo(a)-anthracene
No Load - 1260 rpm	25	68	0.36	0.96
Half Load - 1260 rpm	8	32	0.28	1.10
Full Load - 1800 rpm	16	16	0.63	0.68

[a] Emission rates corrected for POM losses during sample collection and analysis by the use of ^{14}Carbon radioactive tracers.

TABLE 31. TOTAL POM EMISSION FACTORS FOR THE FORD PROTOTYPE DIESEL ENGINE[76]

POM Compound	Without Catalyst[a] (ug/mi)	With Catalyst[b] (ug/mi)	Percent Reduction
Phenanthrene	3.0	0.32	89
Anthracene	0.96	0.064	93
Fluoranthrene	3.7	0.32	91
Pyrene	4.6	2.4	49
Chrysene plus benzo(a)anthracene	11	0.64	94
Perylene	1.9	0.64	66
Benzo(a)pyrene	1.4	0.32	78
Benzo(e)pyrene	4.5	0.64	86
Dibenzopyrenes	0.48	0.32	33
Coronene	0.64	0.48	25
Picene plus dibenzoanthracene	0.8	0.48	40
Benzo(g,h,i)perylene	2.9	N.O.[c]	---
Anthanthrene	1.1	N.O.	---
Others Identified but not Quantified:			
Fluorene, Benzophenanthrene, Benzofluorenes, Benzofluoranthene, Benzo(a)anthracene			
Other Related Emission Measurements:			
Particulate	43-50 mg/km	8-10 mg/km	
Organic extractables	90%	30%	
Free carbon	6%	50%	
Sulfate	4%	20%	

---

[a] Average of four measurements.

[b] Average of two measurements.

[c] N.O. = Not observed.

emit 11,000 ug of benzo(a)pyrene per gallon of oil used.[47] The study theorized that benzo(a)pyrene formation and emissions were a direct function of the oil concentration in the gasoline/oil fuel mixture.[47] No information was provided on the sampling procedures used to derive the emission factor. Therefore, it is not known whether this factor represents particulate, gaseous, or total benzo(a)pyrene.

In the only other identified work on two-cycle engine POM emissions, POM concentrations in chain saw engine exhausts were measured.[59] Concentrations were determined in a laboratory environment and in the field. The sampling procedure used in these tests employed equipment to collect both particulate and gaseous POM. The total POM concentrations were dominated by naphthalene and other two-ring POM compounds. Other POM compounds identified in the exhausts include 2-methylnaphthalene, biphenyl, fluorene, anthracene, pyrene, benz(a)anthracene, benzo(a)pyrene, and benzo(g,h,i)perylene. The typical concentrations of total POM, naphthalene, and benzo(a)pyrene measured in the laboratory chain saw exhausts are as follows.[59]

naphthalene - 14 mg/m^3
total POM - 75 mg/m^3
benzo(a)pyrene - 0.005 mg/m^3

The POM concentrations in the chain saw engine exhausts during the field sampling procedure are given below.[59]

naphthalene - 11 to 22 ug/m^3
total POM - 19 to 42 ug/m^3
benzo(a)pyrene - 0.05 ng/m^3

A comparison of the laboratory and field results shows the field data concentrations to be three to five orders of magnitude less than the laboratory concentrations. This significant difference is attributed to differences in weather and logging conditions during sampling.[59]

Aircraft Turbine Engines--Robertson et al. characterized POM associated with particulate emissions from the combustion of kerosene fuels in a gas turbine engine.[78] The POM compounds identified are shown in Table 32. The majority of the POM found were smaller 3- and 4-fused-ring compounds. Very few 5- and 6-fused-ring compounds were found and those found were in low concentrations. No nitrosamines were found and very few, and low concentrations, of phenols were identified. Polycyclic organic matter concentrations in the exhaust decreased with increasing power settings, while concentrations were higher in exhaust from combustion of lower sulfur fuels. Packed-bed filter studies showed that less than 1 percent of the organic matter emitted by this engine was adsorbed onto particulate matter.

MUNICIPAL, INDUSTRIAL, AND COMMERCIAL WASTE INCINERATION

The bulk of the information available in the literature on POM emissions from waste incineration pertains to municipal solid waste incineration. Consequently, discussions in this part of the document will predominantly concern municipal waste incineration. Industrial and commercial waste incineration is described in relation to POM emissions to the extent possible from readily available literature information.

Process Description

Municipal Waste Incineration--

Municipal wastes are incinerated primarily as a means of volume reduction for eventual waste disposal. Heat energy recovery may also be associated with municipal waste incineration for economic reasons if consumers can be found for the recovered energy. Municipal waste incineration is practiced as a reasonable alternative to the more predominant solid waste disposal method of landfilling. The wastes burned in municipal incineration units come primarily from residential sources;

TABLE 32. POM COMPOUNDS IDENTIFIED BY GC/MS ANALYSIS IN EXHAUST FROM A GAS TURBINE ENGINE BURNING KEROSENE-TYPE FUEL[78]

Fluorene
Anthracene-phenanthrene
Methyl fluorene
Methyl-$C_{14}H_{10}$
Fluoranthene
Pyrene
Aceanthrylene
Benzofluorene
Benzofluoranthene
Chrysene + Napthacene
Benzopyrenes[a]
Perylene

[a] Benzo(a)pyrene and benzo(e)pyrene with most of signal due to benzo(e)pyrene.

however, commercial and industrial sources can in some areas contribute significant quantities to the total waste load. Incineration is a particularly important and useful waste disposal option in space limited areas such as large, densely populated metropolitan cities and cities in coastal zones.

There are two broad categories of incinerators currently used in the United States to perform municipal waste incineration, conventional incinerators and modular or package incinerators. The most significant difference between these categories is the designed waste throughput capacities of typical units. Conventional incinerators are large units that have throughput rates in excess of 45 Mg (50 tons)/day. Conventional units currently in operation have waste throughputs as high as 2,700 Mg (3,000 tons)/day. Modular units are designed to be much smaller in terms of the waste load a single unit can handle. Modular incineration units generally have waste handling capacities of less than 45 Mg (50 tons)/day and the majority are less than 27 Mg (30 tons)/day.[79,80]

Large conventional incinerators generally are more applicable in situations of continuous operation where a large and constant or steady stream or waste material is generated. Disadvantages to using conventional incinerators include a long planning and start-up period before actual operation is realized and a condition of being subject to Federal and State air pollution control regulations (thereby dictating an added cost for overall incinerator installation and operation).

The increased use of modular incinerators for municipal waste disposal is a relatively new trend in the United States that has taken place primarily in the last ten years. A typical, self-contained modular incinerator unit contains the incinerator itself, refuse handling equipment, standard utility connections, and if applicable, emission control equipment. Modular units are designed to be off-the-shelf incinerators that are easily and quickly combined with similar self-contained units of the same given type to enable a facility to increase its waste handling ability without having to purchase a whole new incineration system. Overall, modular units are better suited to handling batch waste disposal operations that are characteristic of sporadic or fluctuating waste material loads.

The majority of existing municipal waste incinerators in the United States use a basic multiple chamber combustion design for waste incineration. These chambers are either refractory-lined or water-walled and are equipped with grates upon which waste is burned. Grates are used to thoroughly mix refuse which helps facilitate more complete combustion. Depending on the particular incinerator design, these grates may be traveling, rocking, circular, or reciprocating. Other design variables that may be incorporated into the basic multiple chamber incinerator include manual or automatic stoking and starved or excess air.[79,80]

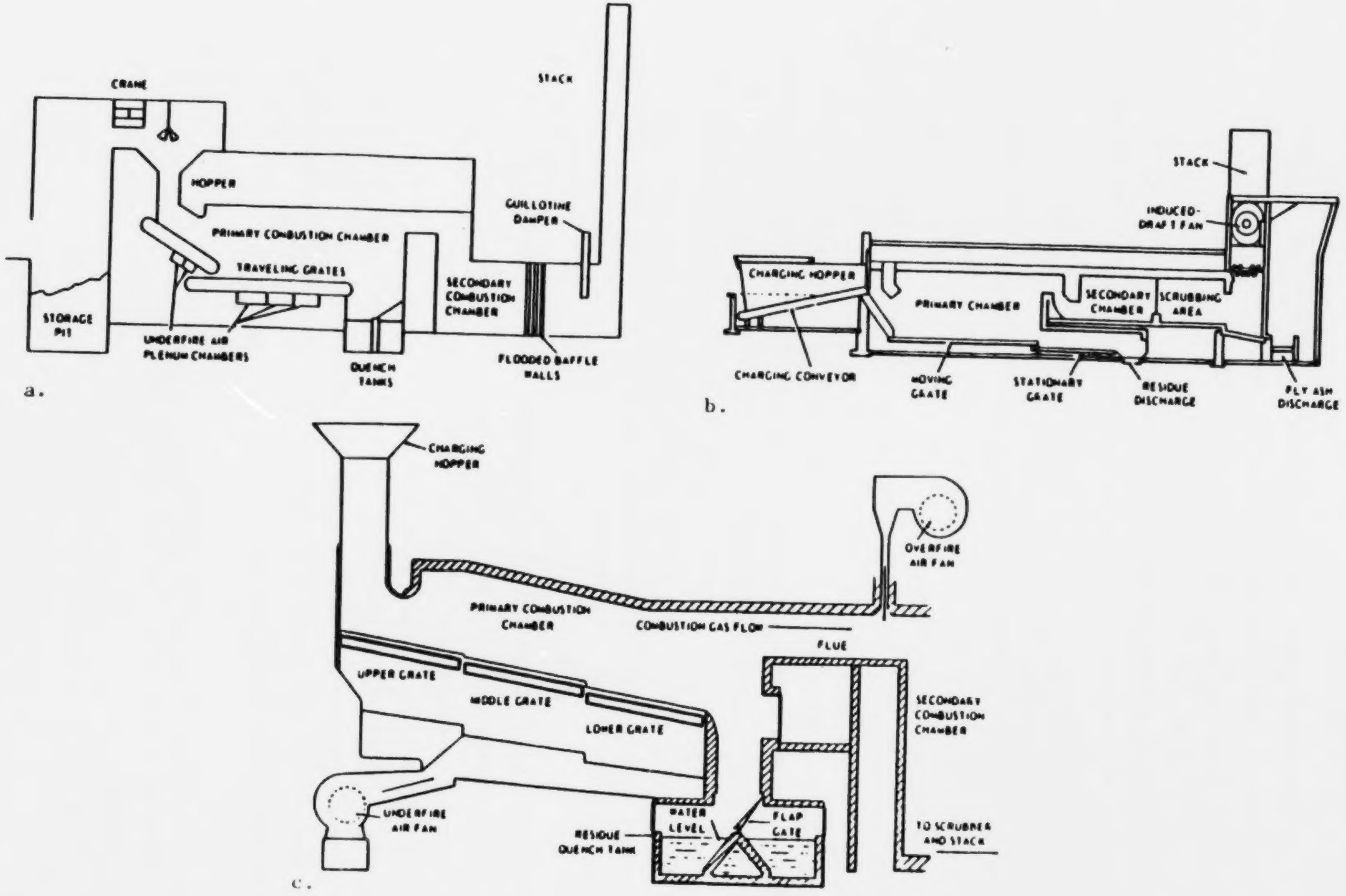
The combustion process in a multiple chamber waste incinerator (conventional or modular) occurs in two stages. The first stage takes place in the primary combusted chamber where the solid waste fuel is dried, ignited, and combusted. This chamber operates with less than stoichiometric amounts of oxygen (i.e., under starved air conditions). In most cases, natural draft or slight induced draft is used to pull air up through the support grate to carry out the primary combustion process. In most conventional and modular municipal waste incineration systems, the temperature immediately above the burning grate in the primary chamber ranges from 760 to 900°C (1400 to 1652°F). The combustion gases from the primary chamber, which are made up of the volatile components of the waste and the products of combustion, are then passed through a flame port connecting the primary chamber to the secondary combustion chamber. The temperature of the gases leaving the primary combustion chamber range from 871 to 982°C (1600 to 1800°F). From the flame port, the heated gases flow into the secondary chamber where secondary air is added for mixing and oxidation purposes. Abrupt changes in the speed and direction of the primary combustion products causes turbulent mixing with the secondary air and more complete oxidation is achieved. Depending on the design of the incinerator, the hot gases exiting the secondary chamber may be either processed to recover their heat energy and then exhausted to a control device or ducted directly to an emission control system.[79,80]

The basic configurations of several conventional municipal waste incinerators are illustrated in Figure 6.[81] Prevalent modular incinerator systems are shown in Figure 7.[81]

Municipal waste incinerators are controlled most commonly by ESPs, baghouses, and wet scrubbers. Very effective particulate matter control can be achieved using ESPs, baghouses, or scrubbers; however, ESPs and baghouses are significantly more efficient at controlling fine particle emissions from incinerators. Scrubbers, however, offer the advantage of providing control for acid gases and sulfur oxide that neither ESPs or baghouses can claim. Afterburners also are used on incinerators as a control measure for organic compound emissions. Conventional incinerators have some form of controls such as these. Modular units may or may not have such controls depending on the size of the unit, the number of units, and existing local regulations. Modular units, when controlled, are typically equipped with ESPs, scrubbers, or afterburners.[80]

Currently, about 75 percent of conventional municipal waste incinerators are controlled by ESPs. Advantages of ESP use include good emissions control, the ability to handle high temperature [above 300°C (570°F)] flue gases, and a continuous operation mode that requires minimal downtime for cleaning and maintenance. Wet scrubbers are used for emissions control on about 20 percent of existing conventional municipal waste incinerators. Generally, scrubbers used for incinerator emissions control will be of one of the following types.[80]

1. low energy (e.g., spray tower)
2. medium energy (e.g., packed column, baffle plate or liquid impingement)
3. high energy (e.g., venturi)



CRANE
STACK
HOPPER
PRIMARY COMBUSTION CHAMBER
TRAVELING GRATES
GUILLOTINE DAMPER
SECONDARY COMBUSTION CHAMBER
STORAGE PIT
UNDERFIRE AIR PLENUM CHAMBERS
QUENCH TANKS
FLOODED BAFFLE WALLS
a.
STACK
INDUCED-DRAFT FAN
CHARGING HOPPER
PRIMARY CHAMBER
SECONDARY CHAMBER
SCRUBBING AREA
CHARGING CONVEYOR
MOVING GRATE
STATIONARY GRATE
RESIDUE DISCHARGE
FLY ASH DISCHARGE
b.
CHARGING HOPPER
OVERFIRE AIR FAN
PRIMARY COMBUSTION CHAMBER
COMBUSTION GAS FLOW
FLUE
UPPER GRATE
MIDDLE GRATE
LOWER GRATE
SECONDARY COMBUSTION CHAMBER
UNDERFIRE AIR FAN
WATER LEVEL
FLAP GATE
RESIDUE QUENCH TANK
TO SCRUBBER AND STACK
c.

Figure 6. Typical configurations of conventional municipal waste incinerators.[81]

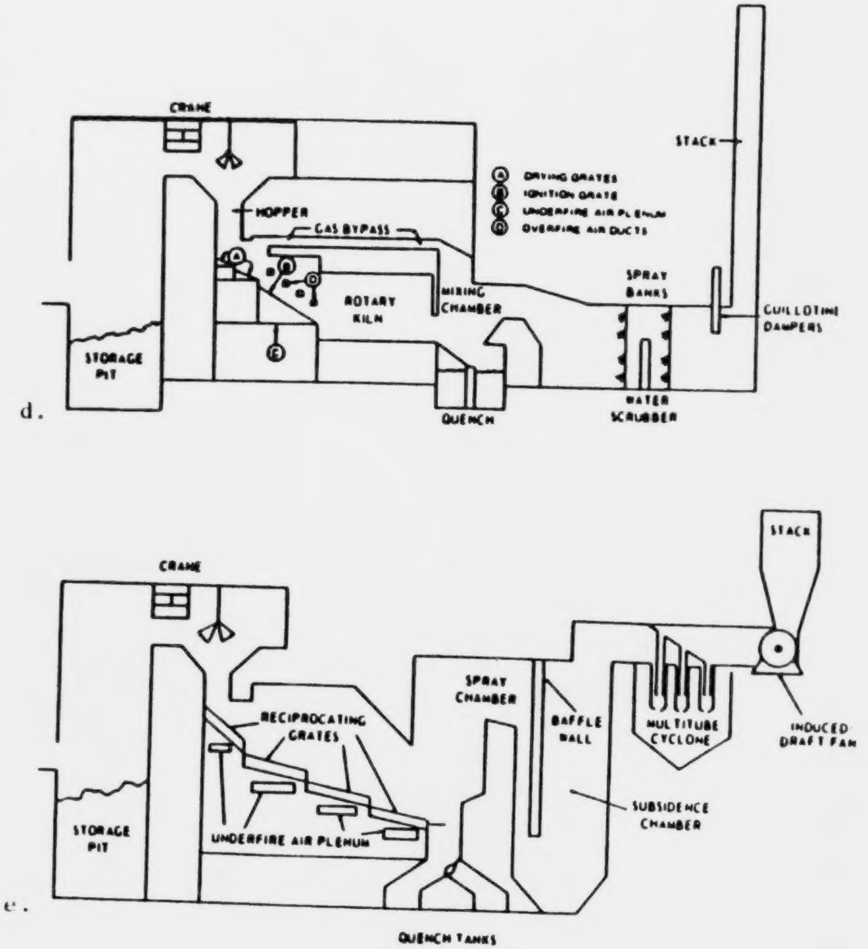
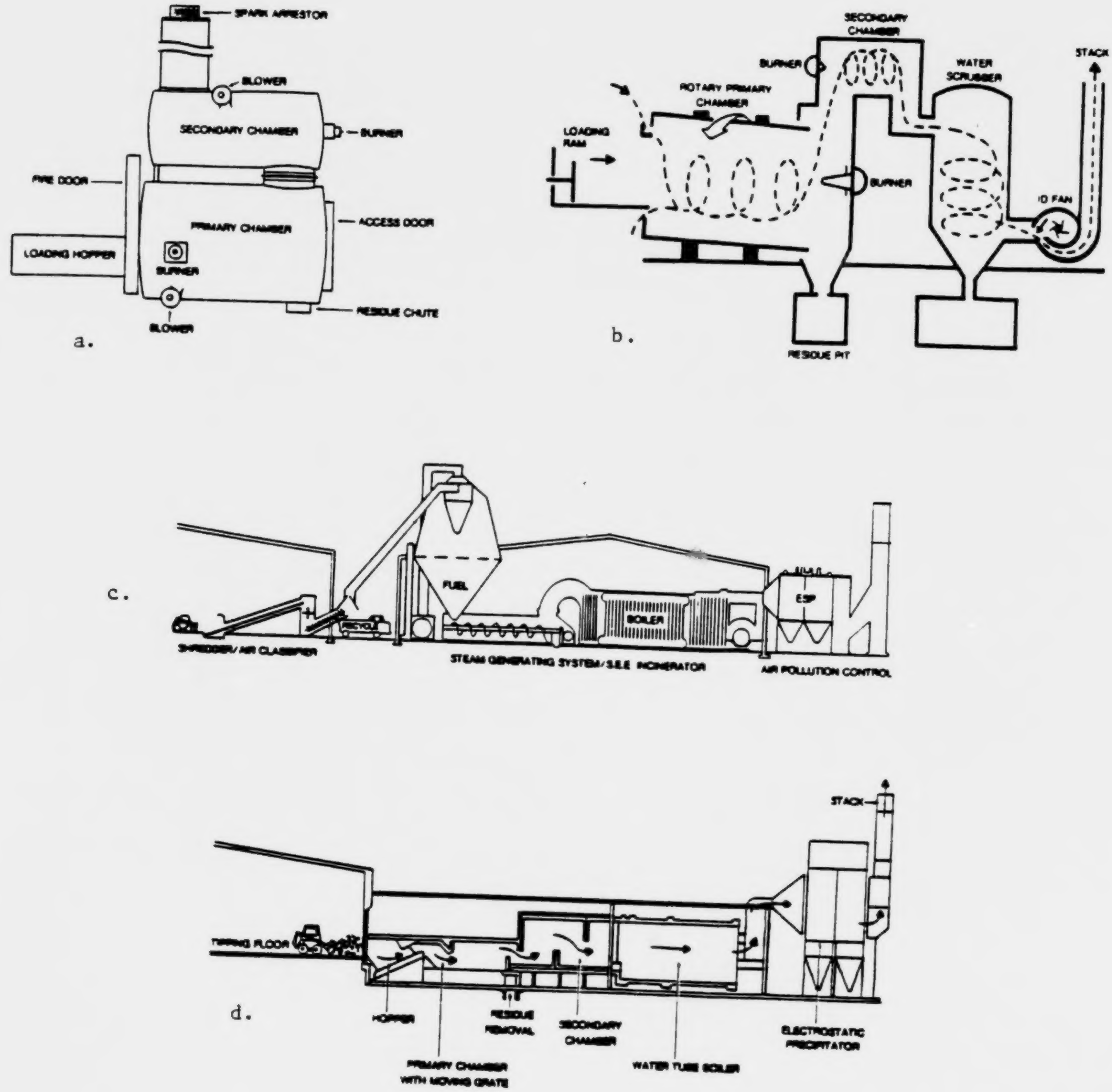

d.
CRANE
HOPPER
GAS BYPASS
STORAGE PIT
ROTARY KILN
MIXING CHAMBER
QUENCH
Ⓐ DRYING GRATES
Ⓑ IGNITION GRATE
Ⓒ UNDERFIRE AIR PLENUM
Ⓓ OVERFIRE AIR DUCTS
SPRAY BANKS
WATER SCRUBBER
STACK
GUILLOTINE DAMPERS
e.
CRANE
STORAGE PIT
RECIPROCATING GRATES
UNDERFIRE AIR PLENUM
SPRAY CHAMBER
BAFFLE WALL
QUENCH TANKS
SUBSIDENCE CHAMBER
MULTITUBE CYCLONE
INDUCED DRAFT FAN
STACK

Figure 6. Typical configurations of conventional municipal waste incinerators (continued).[81]



SPARK ARRESTOR
BLOWER
SECONDARY CHAMBER
BURNER
FIRE DOOR
ACCESS DOOR
PRIMARY CHAMBER
LOADING HOPPER
BURNER
RESIDUE CHUTE
BLOWER
a.
SECONDARY CHAMBER
BURNER
ROTARY PRIMARY CHAMBER
WATER SCRUBBER
STACK
LOADING RAM
BURNER
ID FAN
b.
RESIDUE PIT
c.
FUEL
RECYCLE
BOILER
ESP
SHREDDER/ AIR CLASSIFIER
STEAM GENERATING SYSTEM/ S.E.E. INCINERATOR
AIR POLLUTION CONTROL
STACK
TIPPING FLOOR
d.
HOPPER
RESIDUE REMOVAL
SECONDARY CHAMBER
ELECTROSTATIC PRECIPITATOR
PRIMARY CHAMBER WITH MOVING GRATE
WATER TUBE BOILER

Figure 7. Typical configurations of modular municipal waste incinerators.[81]

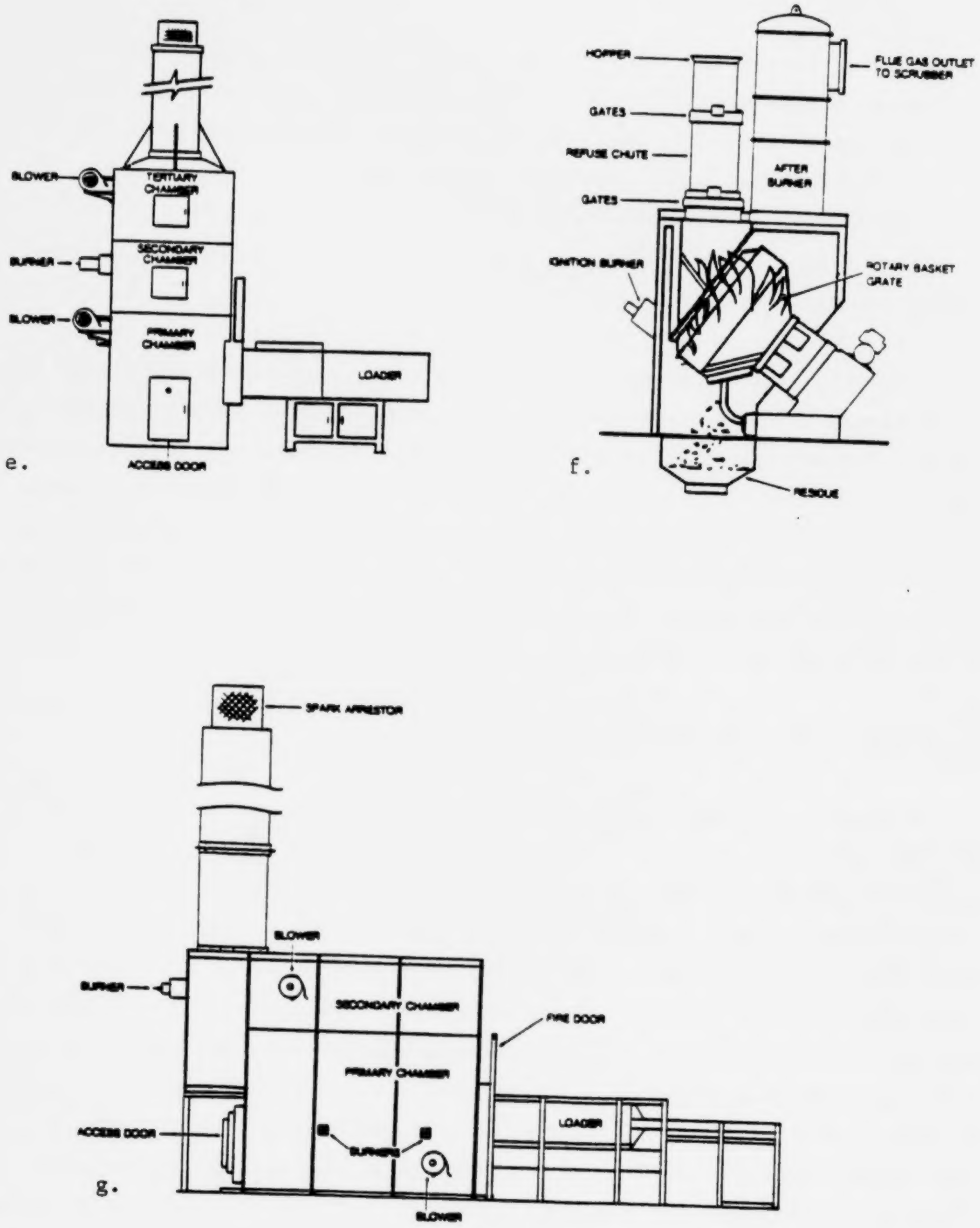

BLOWER
TERTIARY CHAMBER
BURNER
SECONDARY CHAMBER
BLOWER
PRIMARY CHAMBER
LOADER
ACCESS DOOR
e.
HOPPER
GATES
REFUSE CHUTE
GATES
IGNITION BURNER
AFTER BURNER
FLUE GAS OUTLET TO SCRUBBER
ROTARY BASKET GRATE
RESIDUE
f.
SPARK ARRESTOR
BLOWER
BURNER
SECONDARY CHAMBER
FIRE DOOR
PRIMARY CHAMBER
ACCESS DOOR
LOADER
BURNERS
BLOWER
g.

Figure 7. Typical configurations of modular municipal waste incinerators (continued).[81]

Simultaneous particulate matter and gaseous pollutant control and the ability to handle high temperature flue gases are two advantages of wet scrubber use on municipal waste incinerators. One drawback to scrubber use is the need to treat and dispose of contaminated scrubber effluent. The small percentage of conventional municipal waste incinerators not controlled by either ESPs or wet scrubbers are controlled by a mixture of baghouses, baffle chambers, and cyclones.[79,80]

Recently, dry scrubbing systems have been tested on conventional waste incinerators for emissions control. Effective control on particulate matter, including submicron particles, sulfur dioxide, and acid gases was demonstrated using dry scrubbing. Additional benefits of dry scrubbing include minimal system corrosion (a major problem in wet scrubbing systems) and no visible emissions plume (because flue gas is not moisture saturated). Dry scrubbing may become prominent on future municipal waste incinerators should current research continue to be favorable.[80]

Industrial Waste Incineration--

Industrial wastes combusted in incinerators consist primarily of processing wastes and plant refuse and contain paper, plastic, rubber, textiles, and wood. Because of the variety of manufacturing operations, waste compositions are highly variable between plants, but may be fairly consistent within a plant. Industrial waste incinerators are basically the same design as municipal waste incinerators. Available data indicate that approximately 91 percent of the units are multichamber designs, 8 percent are single chamber designs, and 1 percent are rotary kiln or fluidized bed designs. About 1500 of the estimated 3800 industrial incinerators are used for volume reduction, 640 units (largely in the petroleum and chemical industries) are used for toxicity reduction, and the remaining 1700 units are used for resource recovery, primarily at copper wire and electric motor plants.[79]

Most individual waste incinerators are subject to State and local air quality regulations such that these units have varying degrees of emissions control. Most are equipped with afterburners, and newer units may have or be required to obtain scrubbers or ESPs.[79]

Commercial Waste Incineration--

Commercial waste incinerators are used to reduce the volume of wastes from medical facilities, large office and living complexes, schools, and commercial facilities. Small multichamber incinerators are typically used and over 90 percent of the units require firing of an auxiliary fuel. Emission controls are generally not present on commercial units. The inefficient methods of combustion used in the majority of commercial waste incinerators make these units potentially significant POM emission sources.[79]

Polycyclic organic matter emissions from waste incineration are a function of waste composition, incinerator design and operating practices, and incinerator emissions control equipment. Both the incineration of wastes and the combustion of incinerator auxiliary fuel may be sources of POM emissions. Greater organics and moisture content in wastes increase potential POM emissions upon incineration. Incinerator design and operating practices affect waste mixing, residence time in the flame zone, combustion stoichiometry, and other factors that contribute to POM emissions generation. Incinerator emission controls affect POM emissions by determining whether particulate matter and gaseous pollutants are controlled and to what extent. Generally, POM emissions exist in both particulate and gaseous forms, with available data indicating that often gaseous POM emissions predominate. Incinerators with emission controls designed primarily for particulate matter collection may be accomplishing little POM emissions control.

Emission Factors

Available POM emission factor data for municipal and commercial waste incineration sources are given in Table 33.[82-88] Because most of the factors in Table 33 are for different configurations of incinerator type and control device, comparisons between factors and aggregation of the data is not possible. In controlled incinerator situations, emission factors for individual POM compounds range relatively from 0.1 to 1000 mg/Mg, indicating the possible great variability in emissions. Emissions variability is attributable to widely differing waste compositions (including moisture content) being burned, incinerator operating practices, and control device effectiveness. Control device type and effectiveness may be one of the most important and manageable variables in eventual POM emissions from a municipal waste incinerator because existing data indicate that in many cases the bulk of POM emissions are in gaseous form. Control systems not designed for gaseous organic compound removal may not collect a large portion of incinerator POM emissions.

Total POM emission factors in References 82 and 83 may be biased low because naphthalene was not one of the POM compounds analyzed for. Data from Reference 87 indicates that naphthalene can be a significant contributor to total incinerator POM emissions. In many source test cases, naphthalene has not been analyzed for because it is not viewed to be as important (i.e., toxic) as other POM compounds such as benzo(a)pyrene or benzo(a)anthracene.

The test data for commercial waste incinerators in Table 33 indicates that POM emissions are generally greater from commercial sources than from municipal sources (disregarding differences for controls). This apparent trend is probably attributable to commercial units being operated and maintained less efficiently than municipal units, with emphasis not being given to optimizing combustion conditions and waste destruction. In both of the commercial unit tests described in the literature, pyrene and fluoranthene were consistently the predominant POM compounds measured of those analyzed.

TABLE 33. POM EMISSION FACTORS FOR MUNICIPAL WASTE INCINERATORS

Reference	Incinerator Type[a]	Control Device	POMs Measured[b]	Emission Factors (Units of mg/Mg of Waste Burned Except as Indicated)	
				Range	Mean
82	MSW (multiple chamber, traveling grate)	Settling chamber	Benzo(a)pyrene[c]	0.17[d]	---
			Pyrene[c]	17.6[d]	---
			Benzo(e)pyrene[c]	0.75[d]	---
			Coronene[c]	0.53[d]	---
			Fluoranthene[c]	21.6[d]	---
			Total POM	40.4[d]	---
82	MSW (multiple chamber, reciprocating stoker grate)	None	Benzo(a)pyrene[c]	13.5[d]	---
			Pyrene[c]	115[d]	---
			Benzo(e)pyrene[c]	26.5[d]	---
			Benzo(g,h,i)perylene[c]	75[d]	---
			Coronene[c]	33.1[d]	---
			Phenanthrene[c]	39.7[d]	---
			Fluoranthene[c]	10.1[d]	---
			Total POM	312.9[d]	---
82	MSW (multiple chamber, reciprocating stoker grate)	Wet scrubber	Benzo(a)pyrene[c]	0.20[d]	---
			Pyrene[c]	4.6[d]	---
			Benzo(e)pyrene[c]	1.3[d]	---
			Benzo(g,h,i)perylene[c]	1.4[d]	---
			Coronene[c]	1.4[d]	---
			Fluoranthene[c]	7.3[d]	---
			Total POM	16.2[d]	---
83	MSW (single chamber, reciprocating stoker grate)	ESP	Phenanthrene[c]	0.53 - 1.6[h]	1.1[h]
			Fluoranthene[c]	0.13 - 0.24[h]	0.19[h]
			Pyrene[c]	0.38 - 0.47[h]	0.44[h]
			PCBs[c,e]	0.06 - 0.45[h]	0.20[h]
			PCDDs[c,f]	0.20 - 0.24[h]	0.23[h]
			PCDFs[c,g]	2.1 - 2.4[h]	2.3[h]
			Total POM	3.4 - 5.5[h]	4.4[h]

TABLE 33. POM EMISSIO S FOR MUNICIPAL WASTE INCINERATORS (Continued)

Reference	Incinerator Type[a]	Control Device	POMs Measured[b]	Emission Factors (Units of mg/Mg of Waste Burned Except as Indicated) Range	Emission Factors (Units of mg/Mg of Waste Burned Except as Indicated) Mean
84	MSW	None	Fluoranthene	9 - 46.8 ng/m^{3}[h,i]	30.8 ng/m^{3}[h,i]
			Benzo(b)fluoranthene	1.1 - 4.6 ng/m^{3}[h,i]	3.4 ng/m^{3}[h,i]
			Benzo(k)fluoranthene	1.5 - 11.4 ng/m^{3}[h,i]	4.6 ng/m^{3}[h,i]
			Benzo(a)pyrene	0.5 - 10.1 ng/m^{3}[h,i]	5.8 ng/m^{3}[h,i]
84	MSW	ESP	Fluoranthene	20.4 - 80.5 ng/m^{3}[h,i]	44 ng/m^{3}[h,i]
			Benzo(b)fluoranthene	2.4 - 4.7 ng/m^{3},[h,i]	3.9 ng/m^{3}[h,i]
			Benzo(k)fluoranthene	2.0 - 9.6 ng/m^{3}[h]	5.5 ng/m^{3}[h]
			Benzo(a)pyrene	1.1 - 6.0 ng/m^{3}[h]	5.8 ng/m^{3}[h]
85	MSW (fluidized bed)	Unknown	Monochloronaphthalene	0.10 ug/m^{3}[h]	---
			Dichloronaphthalene	2 ug/m^{3}[h]	---
			Trichloronaphthalene	0.10 ug/m^{3}[h]	---
			Monochloroacenaphtylene	6.3 ug/m^{3}[h]	---
			Dichloroacenaphtylene	1.8 ug/m^{3}[h]	---
			Monochlorophenanthrene	8.7 ug/m^{3}[h]	---
			Dichlorophenanthrene	7.6 ug/m^{3}[h]	---
			Monochlorofluoranthene	15 ug/m^{3}[h]	---
			Dichlorofluoranthene	23 ug/m^{3}[h]	---
			Trichlorofluoranthene	4.9 ug/m^{3}[h]	---
			Monochlorobenzanthracene	2.5 ug/m^{3}[h]	---
			Dichlorobenzanthracene	3.3 ug/m^{3}[h]	---
86	MSW (rolling grate)	ESP	Pyrene	0.4 - 7.0[h]	---
			Fluoranthene	0.4 - 4.0[h]	---
87	MSW (single chamber, reciprocating grate)	ESP	Naphthalene[c]	2,000 - 4,894[h]	2,766[h]
			Acenaphthylene[c]	617 - 1,533[h]	1,000[h]
			Acenaphthene[c]	ND - 28[h]	12[h]
			Fluorene[c]	47 - 113[h]	68[h]
			Phenanthrene[c]	660 - 1,192[h]	851[h]
			Fluoranthene[c]	404 - 702[h]	553[h]

TABLE 33. POM EMISSION FACTORS FOR MUNICIPAL WASTE INCINERATORS (Continued)

Reference	Incinerator Type[a]	Control Device	POMs Measured[b]	Emission Factors (Units of mg/Mg of Waste Burned Except as Indicated)	
				Range	Mean
87	MSW (single chamber, reciprocating grate) (continued)	ESP	Pyrene[c]	447 - 1,021[h]	660[h]
			Chrysene[c]	34 - 102[h]	62[h]
			Benzofluoranthene[c]	45 - 450[h]	155[h]
			Dibenz(a,h)anthracene[c]	ND - 0.55[h]	0.11[h]
			Benzo(g,h,i)perylene[c]	ND - 100[h]	26[h]
			PCBs[c,e]	0.6 - 4.7[h]	3.2[h]
			PCDDs[c,f]	3 - 23[h]	11[h]
			PCDFs[c,g]	18 - 120[h]	53[h]
			Total POM	427 - 10,025[h]	6,300[h]
88	MSW (rocking bar grate)	Wet scrubber, ESP	Fluoranthene	2.5[h]	---
			Pyrene	6.8[h]	---
			Benzo(a)anthracene + chrysene	3.1[h]	---
			Benzo(b) + Benzo(k) + Benzo(j)fluoranthene	1.4h	---
			Benzo(a) + Benzo(e)pyrene	0.9[h]	---
			Perylene	0.77[h]	---
			Benzo(g,h,i)perylene	1.8[h]	---
			Indeno(1,2,3-cd)pyrene	0.77[h]	---
			Coronene	0.2[h]	---
			Total POM	18.2[h]	
82	CSW (single chamber)	None	Benzo(a)pyrene[c]	117[d]	---
			Pyrene[c]	706[d]	---
			Benzo(e)pyrene[c]	99.2[d]	---
			Perylene[c]	6.8[d]	---
			Benzo(g,h,i)perylene[c]	198[d]	---
			Anthanthrene[c]	14.6[d]	---
			Coronene[c]	46.3[d]	---
			Anthracene[c]	104[d]	---

TABLE 33. POM EMISSION FACTORS FOR MUNICIPAL WASTE INCINERATORS (Continued)

Reference	Incinerator Type[a]	Control Device	POMs Measured[b]	Emission Factors (Units of mg/Mg of Waste Burned Except as Indicated)	
				Range	Mean
82	CSW (single chamber) (continued)		Phenanthrene[c]	309[d]	---
			Fluoranthene[c]	485[d]	---
			Total POM	2,086[d]	---
82	CSW (multiple chamber with auxilliary gas burner)	None	Benzo(a)pyrene[c]	573[d]	---
			Pyrene[c]	9,261[d]	---
			Benzo(e)pyrene[c]	573[d]	---
			Perylene[c]	132[d]	---
			Benzo(g,h,i)perylene[c]	1,918[d]	---
			Anthanthrene[c]	174[d]	---
			Coronene[c]	463[d]	---
			Anthracene[c]	190[d]	---
			Phenanthrene[c]	130[d]	---
			Fluoranthene[c]	8,600[d]	---
			Total POM	22,014[d]	---
172	MSW (mass burn, waterwall)	ESP	Benzo(a)pyrene	42-54	48
172	MSW (RDF-fired)	ESP	Benzo(a)pyrene	131	---

[a] MSW = municipal solid waste; CSW = commercial solid waste.

[b] Total POM emission factors represent a summation of the POM compounds measured during a particular emission test. They do not necessarily represent the total of all POM compounds actually emitted by a particular source.

[c] These POM compounds were specifically analyzed for during the emission test.

[d] This emission factor represents primarily particulate POM emissions.

[e] PCBs = polychlorinated biphenyls.

[f] PCDDs = polychlorinated dibenzo-p-dioxins.

[g] PCDFs = polychlorinated dibenzofurans.

[h] This emission factor represents both particulate and gaseous POM emissions.

[i] POM emissions were predominantly in gaseous form.

Source Locations

Estimates for the end of 1985 indicate that there are approximately 223 municipal waste incinerators in operation in the United States. Of these 223 units, 109 are conventional and 114 are modular in design. Conventional and modular unit locations and capacities are given in Tables 34 and 35, respectively.[80]

No site specific location information is available for commercial and industrial waste incinerators. Commercial units are generally located in urbanized, metropolitan areas with large concentrations of people. Locations of industrial waste incinerators parallel those of the industries that use them for waste disposal. The lumber and wood products industries, the primary metals industry, and the printing industry are the greatest users of incinerators for waste disposal. Lumber and wood producers are primarily in the Southeast and Northwest. Primary metals plants are predominantly in the Midwest, the Mideast, and the Southwest. The printing industry has an essentially nationwide distribution.[79]

SEWAGE SLUDGE INCINERATION

Process Description

Sewage sludge incineration refers to the oxidation of sludge material generated by wastewater sewage treatment plants. Polycyclic organic matter emissions from sewage sludge incineration potentially originate from the combustion of carbonaceous material in the sludge, from the combustion POM precursors that may exist in the sludge, and from the combustion of supplemental incinerator fuel (typically natural gas or fuel oil).

The most prevalent types of incinerators for sludge oxidation are multiple-hearth and fluidized-bed units. Multiple-hearth incinerators are relatively simple pieces of equipment, consisting of a steel shell lined with refractory. The interior of the incinerator is divided by horizontal

TABLE 34. LOCATIONS OF CONVENTIONAL MUNICIPAL WASTE INCINERATORS IN THE UNITED STATES[80]

Units With Heat Recovery			Units Without Heat Recovery		
Facility Locations	Number of Units	Waste Capacity[a]	Facility Locations	Number of Units	Waste Capacity[a]
Stamford II, CT	1	54 (60)	Susanville, CA	1	87 (96)
Stamford, CT	1	181 (200)	New Canaan, CT	1	98 (108)
Miami, FL	4	2722 (3000)	Washington, DC	6	1089 (1200)
Tampa, FL	4	907 (1000)	Honolulu, HA	2	1089 (1200)
Pinellas County, FL	2	1814 (2000)	East Chicago, IN	2	227 (250)
Savannah, GA	2	454 (500)	Louisville, KY	4	408 (450)
Chicago, IL	4	1089 (1200)	Shreveport, LA	1	181 (200)
Saugus, MA	2	1089 (1200)	Fall River, MA	2	218 (240)
North Andover, MA	2	1361 (1500)	Framingham, MA	2	163 (180)
Baltimore, MD (RESCO)	3	1960 (2160)	Baltimore, MD (Pulaski)	4	1089 (1200)
St. Louis, MO	2	717 (790)	Duluth, MN	2	109 (120)
Oyster Bay, NY	2	1497 (1650)	Brooklyn, NY (SW)	3	680 (750)
Westchester, NY	3	2041 (2250)	Brooklyn, NY (North Henry Street)	1	907 (1000)
Glen Cove, NY	2	204 (225)	Huntington, NY	3	408 (450)
Columbus, OH	6	907 (1000)	Brooklyn, NY (41st Street)	1	680 (750)
Akron, OH	3	177 (195)	North Dayton, OH	2	544 (600)
Marion County, OR	2	499 (550)	South Dayton, OH	2	544 (600)
Harrisburg, PA	2	715 (788)	Philadelphia, PA (East Central)	2	680 (750)
Gallatin, TN	2	181 (200)	Philadelphia, PA (NW)	2	680 (750)
Nashville, TN	2	431 (475)			
Ogden, UT	3	408 (450)			
Hampton, VA	2	272 (300)			
Norfolk, VA	2	163 (180)			
Harrisonburg, VA	2	64 (70)			
Portsmouth, VA	2	73 (80)			
Sheyboygan, WI	2	218 (240)			
Waukesha, WI	2	159 (175)			

[a] Units are Mg (tons)/day of waste that are possible to be burned.

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. From 1986 data base.

TABLE 35. LOCATIONS OF MODULAR MUNICIPAL WASTE INCINERATORS IN THE UNITED STATES

Units With Heat Recovery				Units Without Heat Recovery			
Facility Locations	Number of Units	Waste Capacity[a]		Facility Locations	Number of Units	Waste Capacity[a]	
Sitka, AK	2	45	(50)	Blytheville, AR	2	64	(70)
Huntsville, AL	3	45	(50)	Hot Springs, AR	8	91	(100)
Tuscaloosa, AL	4	290	(320)	Stuttgart, AR	3	34	(37)
Batesville, AR	1	45	(50)	Hope, AR	3	34	(37)
Little Rock, AR	4	91	(100)	Harpswell, ME	1	13	(14)
Osceola, AR	2	45	(50)	Wrightsville, NC	2	27	(30)
Windham, CT	3	98	(103)	Litchfield, NH	1	21	(23)
Mayport, FL	1	44	(48)	Meredith, NH	2	28	(31)
Burley, ID	2	91	(100)	Candia, NH	1	14	(15)
Bancock County, ID	2	181	(200)	Nottingham, NH	1	3.6	(4)
Pittsfield, MA	3	653	(720)	Pittsfield, NH	1	44	(48)
Auburn, ME	4	181	(200)	Wilton, NH	1	27	(30)
Red Wing, MN	1	65	(72)	Wolfeboro, NH	1	34	(37)
Collegeville, MN	1	50	(55)	Auburn, NH	1	4.5	(5)
Ft. Leo. Wood, MO	3	36	(40)	Canterbury, NH	1	9	(10)
Pascagoula, MS	2	136	(150)	Skaneateless, NY	1	11	(12.5)
Livingston, MT	2	64	(70)				
Wilmington, NC	2	94	(104)				
Groveton, NH	1	22	(24)				
Durham, NH	3	98	(108)				
Portsmouth, NH	4	181	(200)				
Niagra Falls, NY	2	2722	(3000)				
Rome, NY	4	181	(200)				
Cattaraugus, NY	3	102	(112.5)				
Volney, NY	4	181	(200)				
Miami, OK	1	65	(72)				
Johnsonville, SC	1	45	(50)				
Lewisburg, TN	1	36	(40)				

TABLE 35. LOCATIONS OF MODULAR MUNICIPAL WASTE INCINERATORS IN THE UNITED STATES (Continued)

Units With Heat Recovery			Units Without Heat Recovery		
Facility Locations	Number of Units	Waste Capacity[a]	Facility Locations	Number of Units	Waste Capacity[a]
Dyersburg, TN	1	74 (82)			
Waxahachie, TX	2	54 (60)			
Gatesville, TX	1	6.4 (7)			
Palestine, TX	1	25 (28)			
Salem, VA	4	91 (100)			
Newport News, VA	1	27 (30)			
Bellingham, WA	8	91 (100)			

[a] Units are Mg (tons)/day of waste that are possible to be burned.

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. From 1986 data base.

brick arches into separate compartments or hearths. Alternate hearths are designed with openings to allow solid material to drop onto the hearth below. At the center of the unit, a shaft rotates rabble arms that are located on each hearth. To enable the incinerated material to move inward and then outward on alternate hearths, teeth on the rabble arms are placed at an angle. As sludge is fed through the roof of the incinerator, the rotating rabble arms and rabble teeth push the material across the hearth to drop holes where it falls to the next hearth. This process continues until the sterile ash produced by the oxidation steps is discharged from the bottom of the incinerator. A schematic diagram of a typical multiple-hearth sewage sludge incinerator is presented in Figure 8.[89]

The majority of multiple-hearth incinerators have three distinct operating zones. The first zone includes the top hearths where the water-laden sludge feed is partially dried by rising hot combustion gases. The second operating zone is the incineration/deodorization zone where temperatures of 760°-980°C (1400-1800°F) are reached and maintained. The third zone of the multiple-hearth unit is the cooling zone where hot ash from incineration releases heat to incoming combustion air.

The second technique used to oxidize sewage sludge is fluidized-bed incineration. Figure 9 represents the basic operations found in a fluidized-bed unit. In this operation, dewatered sludge is introduced into the freeboard area of the incinerator just above the fluidized-bed material (which is usually sand). Air injected through tuyeres at pressures of from 3 to 5 psig fluidize the bed. Hot combustion gases rising from the bed evaporate remaining water in the sludge and sludge solids then enter the fluidized bed. The organic constituents of the sludge are oxidized to carbon dioxide and water vapor which exit the system as exhaust gases. During this reaction, the bed is vigorously mixed and the bed temperature is maintained at 760-927°C (1400-1700°F). Material residence time in the combustion zone is 2 to 5 seconds. Remaining inorganic sludge material either deposits on the bed sand particles and is removed from the bottom of

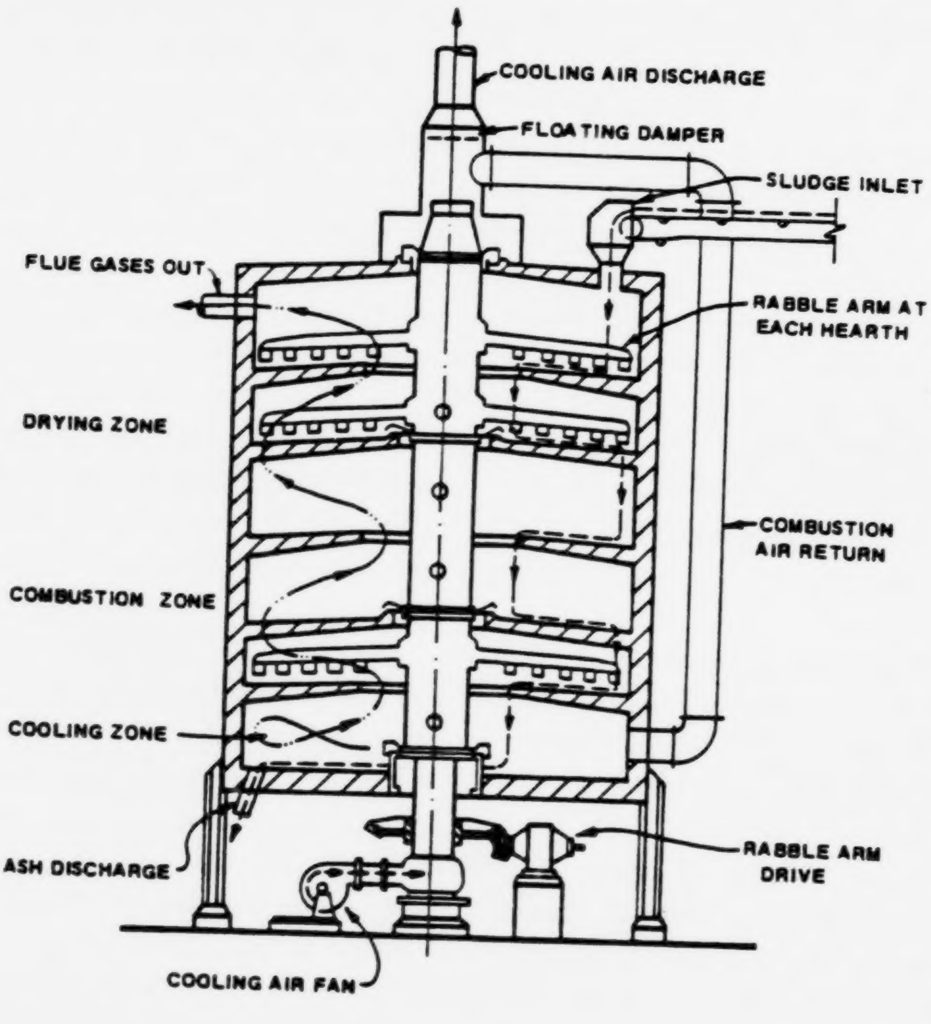

COOLING AIR DISCHARGE
FLOATING DAMPER
SLUDGE INLET
FLUE GASES OUT
RABBLE ARM AT EACH HEARTH
DRYING ZONE
COMBUSTION AIR RETURN
COMBUSTION ZONE
COOLING ZONE
ASH DISCHARGE
RABBLE ARM DRIVE
COOLING AIR FAN

Figure 8. Cross section of a typical multiple-hearth incinerator.[89]

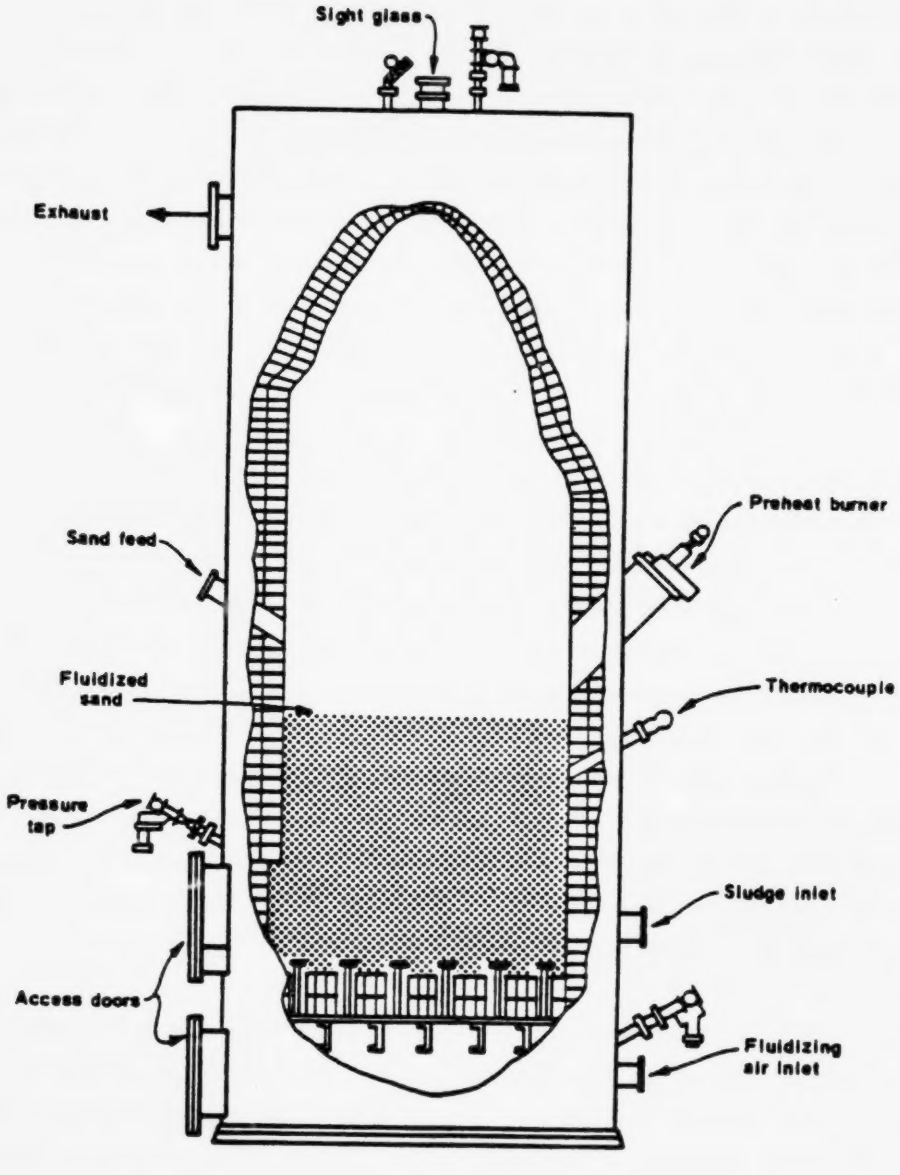

Sight glass
Exhaust
Preheat burner
Sand feed
Fluidized sand
Thermocouple
Pressure tap
Sludge inlet
Access doors
Fluidizing air inlet

Figure 9. Cross section of a fluidized-bed sewage sludge incinerator.[89]

the reactor, or it can be made to exit with the exhaust gases. Air velocity through the bed is used to control the method of inorganic sludge material removal.[89]

Controlling the rate of feed of the sludge into the incinerator is the most critical operating variable for fluidized-bed units. There is an upper limit on the rate of heat transfer that can be achieved for a given quantity of sand. If the rate of sludge feed exceeds the burning capacity of the sand bed, combustion will not be complete. Similarly, either a rapid increase in the overall furnace load or in the total moisture content of the sludge will lead to coagulation of the sludge into heavy masses, depress the bed, and halt combustion. It is also important, for the same reasons, to ensure that an adequate residence time is available for the sludge to burn completely.[89]

Electric incinerators and rotary kilns are also used to destroy sewage sludge, but to a much lesser degree than either multiple-hearth or fluidized-bed units. Electric incinerators consist of a horizontally oriented, insulated furnace. A belt conveyor extends the length of the furnace. Infrared heating elements are located in the roof above the conveyor belt. Combustion air is preheated by the flue gases and is injected into the discharge end of the furnace. To begin the process, dewatered sludge cake is conveyed into one end of the incinerator. An internal roller mechanism levels the sludge into a continuous layer approximately one inch thick across the width of the belt. The sludge is dried and then burns as it moves beneath the infrared heating elements. Ash is discharged into a hopper at the opposite end of the furnace.

The preheated combustion air enters the furnace above the ash hopper and is further heated by the outgoing ash. The direction of air flow is countercurrent to the movement of the sludge along the conveyor. Exhaust gases leave the furnace at the feed end. Electric incinerators consist of a number of prefabricated modules, which can be linked together to provide the necessary furnace length.[89]

Rotary kilns have been applied in systems only requiring limited sludge burning capacity [up to 544 kg (1200 lb)/hr]. The typical kiln is inclined slightly to the horizontal plane, with the upper end receiving both the sludge feed and the combustion air. A burner is located at the opposite end of the kiln. The kiln rotates at a speed of about 6 inches per second, with sludge being combusted as it moves down the kiln. Ash from incineration is deposited into a hopper located below the burner.

Of the known total number of sewage sludge incinerators in the United States, approximately 73 percent are multiple-hearth units, 20 percent are fluidized-bed units, 5 percent are electric incinerators, 1.5 percent are coincineration with municipal solid waste units and less than 1 percent are rotary kilns.[89]

Emissions from sewage sludge incinerators are controlled by various designs of wet scrubbers. Scrubbers have evolved as the preferred method of control for sludge incinerators because: (1) the treatment plant provides a relatively inexpensive source of scrubbing water and a system for treating scrubber effluent and (2) they have been shown to be effective particulate matter emission control systems.

Prior to 1978, sludge incinerator emissions were controlled predominantly by impingement tray, venturi, and venturi/impingement tray scrubbers. A detailed breakdown of controls prior to 1978 for multiple-hearth, fluidized-bed, and electric incinerators is provided in Table 36.[89] After 1978, the dominant emission control system applied to multiple-hearth and fluidized-bed sludge incinerators was venturi/impingement tray scrubbers. Venturi scrubbers were the primary emission control system for electric incinerators. A detailed breakdown of post-1978 sludge incinerator controls is given in Table 37. After 1978, a non-scrubbing system, a baghouse, was also used for emissions control on a sewage sludge incinerator. As shown in Table 37, since 1978, venturi/impingement tray scrubbers are the preferred emissions control technology for sewage sludge incinerators.[89]

TABLE 36. DISTRIBUTION OF EMISSION CONTROL TECHNIQUES APPLIED TO SELECTED SEWAGE SLUDGE INCINERATORS PRIOR TO 1978[89]

Control Type	Applications to Incinerators Percent of Total	Range of Pressure Drops (in. w.g.)
Multiple-Hearth Incinerators		
Impingement Tray	40	6 - 9
Venturi	22	15 - 32
Venturi/Impingement Tray	20	15 - 35
Spray Tower	10	4 - 9
Wet Cyclone	5	3 - 4
Venturi/Wet Cyclone	3	15
Fluidized-Bed Incinerators		
Venturi/Impingement Tray	68	12 - 40
Impingement Tray	23	4
Venturi	9	17 - 18
Electric Incinerators		
Venturi	57	4 - 9
Impingement Tray	29	6 - 9
Venturi/Wet Cyclone	14	12

TABLE 37. DISTRIBUTION OF EMISSION CONTROL TECHNIQUES APPLIED TO SEWAGE SLUDGE INCINERATORS AFTER 1978[89]

Control Type	Applications to Incinerators Percent of Total	Range of Pressure Drops (in. w.g.)
Multiple-Hearth Incinerators		
Venturi/Impingement Tray	88	10 - 45
Fabric Filter	6	---
Impingement Tray	6	10
Fluidized-Bed Incinerators		
Venturi/Impingement Tray	75	42
Venturi	25	Not Reported
Electric Incinerators		
Venturi	75	8 - 10
Venturi/Impingement Tray	25	10

Emission Factors

Tests of air emissions from sewage sludge incinerators have confirmed the existence of POM compounds from this source category; however, quantitative POM emission factors are limited. The only POM emission factors found in the literature for sewage sludge incinerators are presented in Table 38.[90] The seven POM compounds listed in Table 38 were specifically analyzed for during the emission tests.

In tests of another sludge incinerator equipped with a wet scrubber control device, 20 different POM compounds were detected. A list of these 20 is provided in Table 39.[91] The predominant POM compounds found in sludge incinerator exhausts were phenanthrene, fluoranthene, fluorene, and pyrene. The sampling technique used during the tests of the sludge incinerator measured both particulate and gaseous POM. The greatest proportion of the POM emissions were consistently found to be in a gaseous state.

Source Locations

According to a 1985 U. S. EPA assessment, approximately 266 sewage sludge incinerators are in existence in the United States. The distribution of these 266 by type is as follows.[92]

- multiple hearth - 195
- fluidized bed - 54
- electric - 12
- rotary kiln - 2
- municipal solid waste co-combustion - 3

Of the 266, 155 units are estimated to be in operation. The breakdown of operating units within each major incinerator type is given below.

- multiple hearth - 119
- fluidized bed - 25

TABLE 38. POM EMISSION FACTORS FOR A SEWAGE SLUDGE INCINERATOR CONTROLLED BY A WET SCRUBBER

POM Compound	POM Emission Factor, g/Mg (lb/ton)[a,b,c]
Acenaphthylene	0.12 - 0.16 (0.00024 - 0.00032)
Pyrene	0.17 - 0.25 (0.00034 - 0.00050)
Fluorene	0.38 - 0.41 (0.00076 - 0.00082)
Carbazole	0.09 - 0.21 (0.00018 - 0.00042)
Fluoranthene	0.81 (0.0016)
Benzo(a)pyrene	0.002 - 0.007 (0.000004 - 0.000014)
Dibenzofuran	1.1 - 1.3 (0.0022 - 0.0026)

[a] Emission factors are expressed in terms of g (lb) POM emitted per Mg (ton) of dry sludge fed to the incinerators. The range given is for two emission test runs.

[b] Emission factors represent the joint final stack emissions of a sewage sludge incineration facility containing two incinerators, each controlled by a wet scrubber. Scrubber exhausts are funneled to a single stack for atmospheric release.

[c] The sampling and analysis procedures used during these tests resulted in both particulate and gaseous POM being measured.

TABLE 39. POM COMPOUNDS IDENTIFIED IN SEWAGE SLUDGE INCINERATOR EMISSIONS[91]

Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Chrysene
Triphenylene
Benzo(g,h,i)fluoranthene
Benzo(a)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
O-phenylene pyrene
Dibenzo(a,c)anthracene
Dibenzo(a,h)anthracene
Benzo(b)chrysene
Benzo(g,h,i)perylene
Anthanthrene

- electric - 8
- rotary kiln - 1
- municipal solid waste co-combustion - 2

A State-by-State distribution of the number of total and operating sewage sludge incinerators by type is given in Table 40.[92] The States where sewage sludge incineration is predominantly practiced are New York, Michigan, Connecticut, Pennsylvania, New Jersey, Ohio, Virginia, and California.

A list of wastewater treatment plants where sludge incineration is thought to be practiced is given in Table 41.[93,94] Because the list of facilities in Table 41 was developed at a different time and by a different group than that which developed the sludge facility distribution data in Table 40, the total number of facilities shown in the two tables differ slightly.

PETROLEUM CATALYTIC CRACKING - CATALYST REGENERATION

Process Description

Catalytic cracking processes currently serve a major role in modern petroleum refineries by substantially increasing the production of gasoline from a given amount of crude oil. This increased production is accomplished by cracking heavier feedstocks such as atmospheric or vacuum gas oils to produce slurry oil, light cycle oil, cracked gasoline, light gases, and coke.[95] Catalytic cracking takes place in the presence of a catalyst which can become deactivated through the continual deposition of carbon, in the form of coke, on active sites. To combat catalyst degradation, catalysts are regenerated by combusting the coke deposits on the catalyst. This combustion of coke or catalyst regeneration process has been found to form POM emissions, and thus makes catalytic cracker catalyst regenerators potential POM emission sources.[96,97]

TABLE 40. APPROXIMATE DISTRIBUTION OF SLUDGE COMBUSTION FACILITIES BY STATE AND TYPE IN 1985[92]

State	Multiple Hearth		Fluidized Bed		Electric (Infrared)		Rotary Kiln		Co-combustion		State Totals	
	Total	Operating	Total	Operating	Total	Operating	Total	Operating	Total	Operating	Total	Operating
Alaska	2	1	0	0	2	1	0	0	0	0	4	2
Arkansas	1	0	2	1	0	0	0	0	0	0	3	1
California	9	5	5	2	0	0	1	1	0	0	15	8
Colorado	1	0	0	0	0	0	0	0	0	0	1	0
Connecticut	13	8	4	1	0	0	0	0	1	1	18	10
Florida	2	1	0	0	0	0	0	0	0	0	2	1
Georgia	4	4	0	0	2	2	0	0	1	1	7	7
Hawaii	2	1	0	0	0	0	0	0	0	0	2	1
Illinois	4	1	0	0	0	0	0	0	0	0	4	1
Indiana	2	1	1	1	0	0	0	0	0	0	3	2
Iowa	2	2	1	1	0	0	0	0	0	0	3	3
Kansas	2	2	2	2	0	0	0	0	0	0	4	4
Kentucky	2	0	0	0	1	1	0	0	0	0	3	1
Louisiana	3	3	1	1	0	0	0	0	0	0	4	4
Maryland	5	2	1	1	0	0	0	0	0	0	6	3
Massachusetts	9	4	2	0	0	0	1	0	0	0	12	4
Michigan	20	10	2	1	1	0	0	0	0	0	23	11
Minnesota	2	2	0	0	0	0	0	0	0	0	2	2
Missouri	2	1	3	0	0	0	0	0	0	0	5	1
Nebraska	0	0	1	1	0	0	0	0	0	0	1	1
Nevada	2	0	1	0	0	0	0	0	0	0	3	0
New Hampshire	3	3	0	0	0	0	0	0	0	0	3	3
New Jersey	11	10	6	5	0	0	0	0	0	0	17	15

TABLE 40. APPROXIMATE DISTRIBUTION OF SLUDGE COMBUSTION FACILITIES BY STATE AND TYPE IN 1985[92] (Continu

State	Multiple Hearth		Fluidized Bed		Electric (Infrared)		Rotary Kiln		Co-combustion		State Tota	
	Total	Operating	Total	Operating	Total	Operating	Total	Operating	Total	Operating	Total	Operati
New York	30	20	10	3	1	1	0	0	1	0	42	24
North Carolina	2	0	2	1	0	0	0	0	0	0	4	1
Ohio	12	10	2	0	0	0	0	0	0	0	14	10
Oklahoma	2	0	0	0	0	0	0	0	0	0	2	0
Oregon	1	1	0	0	0	0	0	0	0	0	1	1
Pennsylvania	17	9	5	2	0	0	0	0	0	0	22	11
Rhode Island	3	0	0	0	0	0	0	0	0	0	3	0
South Carolina	2	2	0	0	0	0	0	0	0	0	2	2
Tennessee	4	3	1	1	0	0	0	0	0	0	5	4
Texas	1	0	0	0	4	2	0	0	0	0	5	2
Virginia	10	9	1	0	0	0	0	0	0	0	11	9
Washington	1	1	1	1	1	1	0	0	0	0	3	3
West Virginia	2	1	0	0	0	0	0	0	0	0	2	1
Wisconsin	5	2	0	0	0	0	0	0	0	0	5	2
TOTALS	195	119	54	25	12	8	2	1	3	2	266	155

TABLE 41. LOCATIONS OF WASTEWATER TREATMENT PLANTS THOUGHT TO BE USING SEWAGE SLUDGE INCINERATORS[93,94]

Incinerator Locations	POTW Name
Multiple-Hearth Units	
Anchorage, AK	Point Woronzof STP
Palo Alto, CA	Palo Alto WWTF
San Mateo, CA	Not Reported
South Lake Tahoe, CA	South Tahoe WWTF
Truckee, CA	Tahoe-Truckee WWTF
Martinez, CA	Not Reported
Redwood City, CA	Not Reported
San Clemente, CA	San Clemente WWTF
Cromwell, CT	MDC WPCF
Hartford, CT	Hartford WPCF
Killingly, CT	Killingly WPCF
Naugatuck, CT	Naugatuck WPCF
New Haven, CT	East Shore WPCF
New Haven, CT	Boulevard WPCF
New London, CT	New London WPCF
Norwalk, CT	Norwalk WPCF
Waterbury, CT	Waterbury WPCF
Willimantic, CT	Willimantic WPCF
Jacksonville, FL	Buckman Street STP
Pensacola, FL	Main Street Plant
Atlanta, GA	R. M. Clayton
Atlanta, GA	Utoy Creek
Cobb County, GA	Chattahoochee
Savannah, GA	President Street WPCF
Marietta, GA	Not Reported
Honolulu, HI	Sand Island WWTF
Honouliuli, HI	Honouliuli WWTP
Oahu, HI	Not Reported
Decatur, IL	Decatur STP
Rock Falls, IL	Rock Falls STP
Rockford, IL	Rockford S.D. STP

TABLE 41. LOCATIONS OF WASTEWATER TREATMENT PLANTS THOUGHT TO BE USING SEWAGE SLUDGE INCINERATORS[93,94] (Continued)

Incinerator Locations	POTW Name
East Chicago, IN	East Chicago STP
Indianapolis, IN	Belmont Street Plant
Indianapolis, IN	Southport WWTP
Cedar Rapids, IA	Cedar Rapids WPCF
Davenport, IA	Davenport WWTP
Johnson County, KS	Mission Township STP (Main Sewer District No. 1)
Shawnee Mission, KS	Turkey Creek MSD #1
Kenton County, KY	Not Reported
Algiers, LA	New Orleans W. Bank STP
Lake Charles, LA	Plant C
Lake Charles, LA	Plant B
Annapolis, MD	Annapolis City STP
Baltimore, MD	Patapsco WWTP
Riviera Beach, MD	Cox Creek WWTP
Attleboro, MA	Attleboro WWTW
Chicopee, MA	Chicopee WWTP
Fall River, MA	Fall River STP
Fitchburg, MA	Fitchburg East WWTP
Lawrence, MA	Greater Lawrence SD WWTP
New Bedford, MA	New Bedford WWTP
Quincy, MA	Nut Island WWTP
Worcester, MA	Upper Blackstone Reg WWTP
Ann Arbor, MI	Ypsi Community WWTP
Ann Arbor, MI	Ann Arbor WWTP
Bay City, MI	Bay City STP
Bay County, MI	Bay County STP
Battle Creek, MI	Not Reported
Detroit, MI	Detroit STP
East Lansing, MI	East Lansing WWP
Flint, MI	Flint WPCF
Grand Rapids, MI	Grand Rapids
Kalamazoo, MI	Kalamazoo QQTP
Lansing, MI	Lansing WWTP
Niles, MI	Niles Wastewater Treatment Plant
Owosso, MI	Owosso WWTP

TABLE 41. LOCATIONS OF WASTEWATER TREATMENT PLANTS THOUGHT TO BE USING SEWAGE SLUDGE INCINERATORS[93,94] (Continued)

Incinerator Locations	POTW Name
Pontiac, MI	Pontiac STP
Trenton, MI	Trenton WWTP
Warren, MI	Warren WWTP
Wayne County, MI	Wyandotte STP
Eagan, MN	Seneca Treatment Plant
St. Paul, MN	Metropolitan TP
St. Louis, MO	Bissell Point STP
St. Louis, MO	Lemay STP
Kansas City, MO	Kansas City Big Blue River STP
Zephyr Cove, NV	Douglas County SID #1 WWTF
Lebanon, NH	Lebanon WWTF
Merrimack, NH	Merrimack WWTP
Manchester, NH	Manchester WWTP
Atlantic City, NJ	Atlantic County SA
Bridgewater, NJ	Somerset-Raritan
Jersey City, NJ	West Side STP
Parsippany-Troy Hills, NJ	Rockaway Val Regn S A TRT
Princeton, NJ	Stony Brook RSA STP #1
Union Beach, NJ	Bayshore Regional STP
Wayne Township, NJ	Mountain View STP
Albany, NY	South Albany STP
Amherst, NY	Not Reported
Babylon, NY	Southeast SD #3
Beacon, NY	Beacon WPCP
Buffalo, NY	Birds Island STP
Dunkirk, NY	Dunkirk STP
Greece, NY	N W Quadrant TP
Mamaroneck, NY	Mamaroneck San. Sew. District
Menands, NY	North Albany STP
Mechanicville, NY	Saratoga SD #1
New Rochelle, NY	New Rochelle SD STP
New Windsor, NY	New Windsor STP
Orangeburg, NY	Orangetown DPW
Ossining, NY	Ossining SD
Oswego, NY	East STP

TABLE 41. LOCATIONS OF WASTEWATER TREATMENT PLANTS THOUGHT TO BE USING SEWAGE SLUDGE INCINERATORS[93,94] (Continued)

Incinerator Locations	POTW Name
Oswego, NY	West STP
Port Chester, NY	Port Chester SD STP
Rochester, NY	Gates Chili Ogden STP
Rochester, NY	Frank E. Van Lare WWTP
Schenectady, NY	Schenectady STP
Southampton, NY	Disposal District No. 15
Tonawanda, NY	Two Mile Creek SD Plant 2
Utica, NY	Oneida County WPCP
Wheatfield, NY	Niagara CO SD #1 STP
Greensboro, NC	North Buffalo WTP
Rocky Mount, NC	Rocky Mount WWTP
Akron, OH	Akron WWTP
Canton, OH	Canton WWTP
Cincinnati, OH	Millcreek WWTP
Cincinnati, OH	Little Miami WWTP
Cleveland, OH	Westerly WWTP
Cleveland, OH	Southerly WWTP
Columbus, OH	Jackson Pike WTP
Columbus, OH	Columbus-Southerly WWTP
Euclid, OH	Euclid WWTP
Youngstown, OH	Youngstown WWTP
Tigard, OR	Durham Regional STP
Ambridge, PA	Ambridge STP
Apollo, PA	Kiski Valley WPCA
Bridgeport, PA	Bridgeport STP
Chester, PA	Delcora Chester STP
Colmar, PA	Hatfield Township STP
Erie, PA	Erie City STP
Hershey, PA	Derry Township WPCP
Johnstown, PA	City of Johnstown
Norristown, PA	E. Norriton Plymouth TP
North Wales, PA	Upper Gwynedd Township STP
Old Forge, PA	Lower Lackawanna STP
Pittsburgh, PA	Alcosan WWTP
West Hazelton, PA	Greater Hazelton STP
Wilkes-Barre, PA	Wyoming Valley San. Authority
Willow Grove, PA	Upper Moreland-Hatboro TP
York, PA	York WPCC
Lemoine Borough, PA	Cumberland City

TABLE 41. LOCATIONS OF WASTEWATER TREATMENT PLANTS THOUGHT TO BE USING SEWAGE SLUDGE INCINERATORS[93,94] (Continued)

Incinerator Locations	POTW Name
Cranston, RI	Cranston WPCF
Charleston, SC	Plum Island TRT Plant
Columbia, SC	Metropolitan TRT Plant
Bristol, TN	Galloway Mill Plant
Maryville, TN	Maryville Regional STP
Nashville, TN	Nashville Central WWTP
Newport, TN	Newport WWTP
Alexandria, VA	Alexandria STP
Arlington, VA	Arlington County WPCP
Blacksburg, VA	Lower Straubles STP
Fairfax, VA	Lower Potomac STP
Newport News, VA	Boat Harbor WPCF
Norfolk, VA	Lamberts Point WPCF
Norfolk, VA	Army Base WPCF
Virginia Beach, VA	Chesapeake-Elizabeth WPCF
Williamsburg, VA	Williamsburg WPCF
Woodbridge, VA	Potomac River STP
Bellingham, WA	Bellingham Plant
Vancouver, WA	Vancouver Westside STP
Clarksburg, WV	Clarksburg STP
Brookfield, WI	Brookfield STP
DePere, WI	DePere WWTP
Green Bay, WI	Green Bay WWTP
Milwaukee, WI	South Shore Waste Water TP
Fluidized-Bed Units	
North Little Rock, AR	Faulkner Lake STP
San Bernardino, CA	San Bernardino WWTP #2
South Bayside, CA	South Bayside WWTP
Redwood City, CA	Not Reported
Barstow, CA	Barstow Regional WWTP
Stratford, CT	Stratford WPCF

TABLE 41. LOCATIONS OF WASTEWATER TREATMENT PLANTS THOUGHT TO BE USING SEWAGE SLUDGE INCINERATORS[93,94] (Continued)

Incinerator Locations	POTW Name
Elkart, IN	Elkart WWTF
Dubuque, IA	Dubuque WWTP
Kansas City, KS	Not Reported
Kansas City, KS	KCK WWTP #1 - KAW Point
New Orleans, LA	New Orleans East Bank
Ocean City, MD	Ocean City WWTP
Lynn, MA	Lynn Regional WPCP
Port Huron, MI	Port Huron STP
Duluth, MN	WLSSD Regional WWTF
Independence, MO	Not Reported
Omaha, NE	Papillion Creek
Somerset-Raritan, NJ	Not Reported
Two Bridges, NJ	Fairfield Sewer Authority
Union Beach, NJ	Not Reported
Waldwick, NJ	N.W. Bergen
West Bedford, NJ	Not Reported
Hamburg, NY	Southtowns STP
Port Washington, NY	Port Washington STP
Poughkeepsie, NY	Arlington SD
Shelby, NC	Not Reported
Hazelton, PA	Hazelton STP
King of Prussia, PA	Trout Run WPC
Tyrone, PA	Tyrone Borough STP
Clarksville, TN	Clarksville Main WWTP
Edmonds, WA	Edmonds STP

TABLE 41. LOCATIONS OF WASTEWATER TREATMENT PLANTS THOUGHT TO BE USING SEWAGE SLUDGE INCINERATORS[93,94] (Continued)

Incinerator Locations	POTW Name
Electric Units	
Wrangell, AK	Wrangell WWTP
Decatur, GA	Snapfinger WWTP
Gainesville, GA	Flat Creek WPCP
Cynthiana, KY	Not Reported
Bay County, MI	Not Reported
Sylvan Beach, NY	East Oneida Lake WPCP
Fayetteville, NC	Cross Creek Plant
Greenville, TX	Greenville STP
Aberdeen, WA	Aberdeen STP
Rotary Kiln Units	
Lake Arrowhead, CA	Lake Arrowhead WWTF
Los Angeles, CA	Hyperion WWTP
Hopewell, VA	Hopewell STP
Combination Sludge/ Municipal Waste Units	
New Canaan, CT	New Canaan WPCF
Stamford, CT	Stamford WPCF
Glen Cove, NY	Glen Cove STP
Harrisburg, PA	Harrisburg, STP
Other Sludge Units	
Rockville, CT	Vernon WPCF
Lyons, KS	Lyons STP

TABLE 41. LOCATIONS OF WASTEWATER TREATMENT PLANTS THOUGHT TO BE USING SEWAGE SLUDGE INCINERATORS[93,94] (Continued)

Incinerator Locations	POTW Name
St. Charles, MO	St. Charles Miss. River STP
Independence, MO	Rock Creek WWTP
Meadow Grove, NE	Meadow Grove WWTP
Tangier, VA	Tangier STP

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. From 1986 reference.

Three types of catalytic crackers have been used in the petroleum industry: fluid-bed catalytic cracking (FCC) units, Thermofor catalytic cracking (TCC) units, and Houdriflow catalytic cracking (HCC) units. Thermofor and Houdriflow crackers are both moving bed designs. Fluid-bed catalytic crackers greatly dominate over the other two cracking unit types. As of 1979, FCC units constituted 94 percent of total cracking feed capacity, TCC units 5 percent, and HCC units 1 percent.[95] With the advent of new and better catalysts, major design and operational changes have been incorporated in FCC units in recent years. By contrast, no major changes in moving bed type units have been observed and generally TCC and HCC units are being phased out.[95]

A process flow diagram of a typical FCC unit is shown in Figure 10.[95] In the FCC process, hot regenerated catalyst, mixed with hydrocarbon feed, is transported into the cracking reactor. The reactor, which is maintained at about 482°C (900°F) and 15 psig, contains a bed of powdered silica-alumina type catalyst which is kept in a fluidized state by the flow of vaporized feed material and steam.[95,97] Cracking of the feed, which occurs in the riser leading to the reactor and in the fluidized bed, causes a deposit of coke to form on the catalyst particles. A continuous stream of spent catalyst is withdrawn from the reactor and steam stripped to remove hydrocarbons. The catalyst particles are then pneumatically conveyed to a catalyst regeneration unit. Hydrocarbon vapors from the cracking process are fractionated in a distillation column to produce light hydrocarbons, cracked gasoline, and fuel oil.[95]

In the catalyst regeneration unit, coke deposits are burned off at temperatures near 538°C (1000°F) and pressures ranging from 2 to 20 psig.[97] This coke combustion process is the source of POM emissions in regeneration units.[95-97] The regenerated catalyst is continuously returned to the cracking reactor. Heat added to the catalyst during regeneration (coke combustion) furnishes much of the required heat for the cracking reaction.[95] Regenerator flue gases, high in carbon monoxide and unburned hydrocarbons (including potentially POM compounds) are vented to a carbon monoxide waste

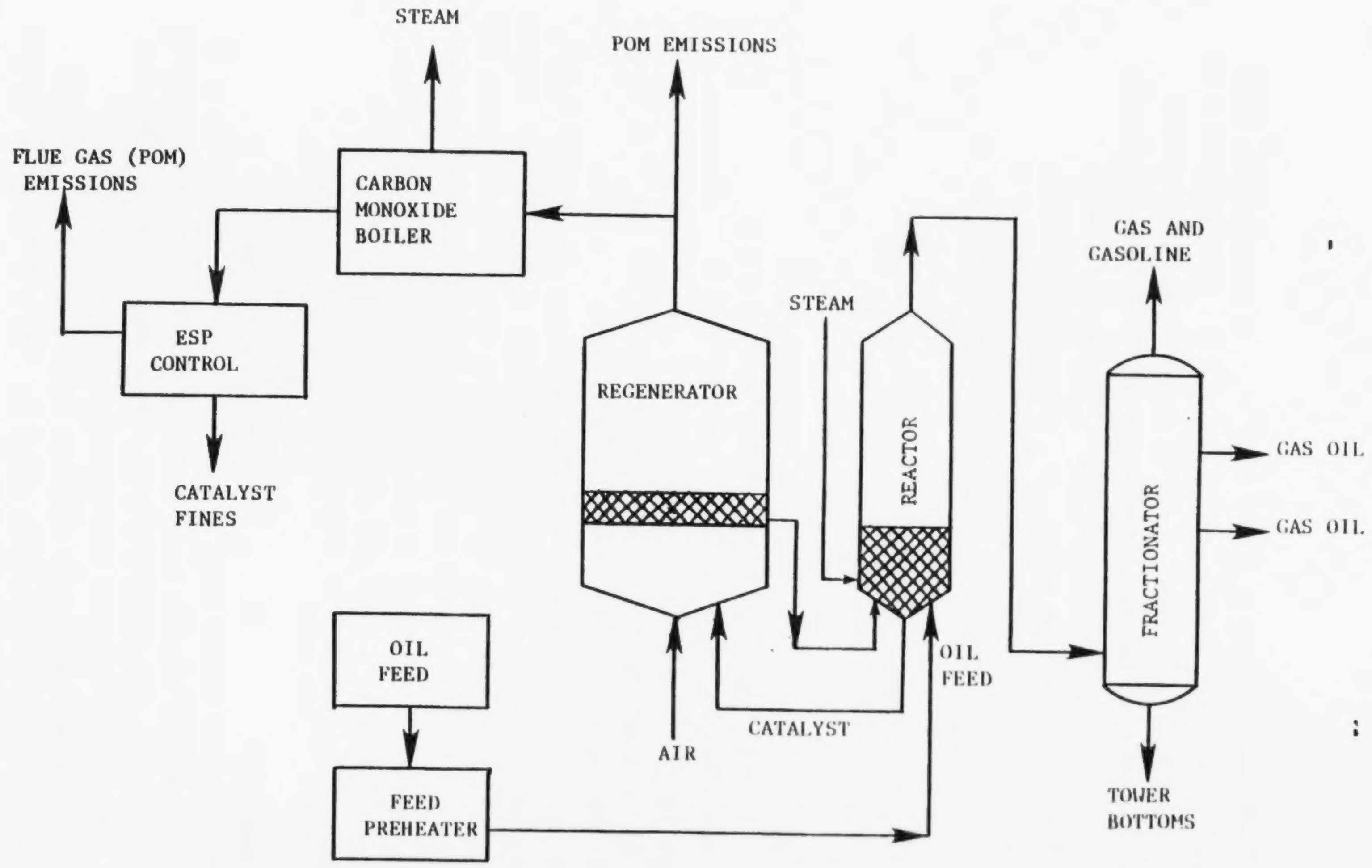

STEAM
POM EMISSIONS
FLUE GAS (POM) EMISSIONS
CARBON MONOXIDE BOILER
ESP CONTROL
CATALYST FINES
REGENERATOR
STEAM
REACTOR
GAS AND GASOLINE
FRACTIONATOR
GAS OIL
GAS OIL
OIL FEED
FEED PREHEATER
AIR
CATALYST
OIL FEED
TOWER BOTTOMS

Figure 10. Diagram of a fluid-bed catalytic cracking process.[97]

heat boiler or directly to the atmosphere.[95,97] Waste heat boilers which are fired with an auxiliary fuel or contain a catalyst are reported to have been 99 percent efficient in reducing PAH emissions from a regeneration unit.[95] In several installations, particulate matter emissions from the waste heat boiler are controlled by an ESP.[95] Catalytic cracking units constructed after June 1973 are subject to a new source performance standard that limits carbon monoxide and particulate matter emissions to such a level that a waste heat boiler and ESP are generally required for compliance.[95]

Thermofor and Houdriflow cracking units, illustrated in Figures 11 and 12, operate similarly to FCC units but use beaded or pelleted catalysts.[95,97] In both TCC and HCC, the cracking process is initiated by having regenerated catalyst and vaporized hydrocarbon feed enter the top of the cracking reactor chamber and travel co-currently downward through the vessel. As the cracking process proceeds, synthetic crude product is withdrawn and sent to the synthetic crude distillation tower for processing into light fuels, heavy fuels, catalytic gasoline, and wet gas.[95] At the base of the reactor, the catalyst is purged with steam to remove hydrocarbons and is then gravity fed into the catalyst regeneration chamber. In the regeneration chamber, combustion air is added at a controlled rate to burn off catalyst coke deposits. As in FCC units, coke burning produces POM emissions that are released in TCC and HCC catalyst regenerator flue gases. Regenerated catalyst is collected at the bottom of the chamber and is conveyed by airlift to a surge hopper above the cracking reactor where it can be gravity fed back into the cracking process.[95]

Flue gases from TCC and HCC units are also either vented directly to the atmosphere or to a carbon monoxide waste heat boiler. Thermofor units have also been equipped in some installations with direct-fired afterburners called plume burners. The plume burner is a secondary stage of combustion built into the catalyst regeneration chambers. This type of burner successfully increases the clarity of plumes from regeneration flue gases; however, compared to a carbon monoxide waste heat boiler, the plume burner is ineffective at reducing POM emissions.[97]

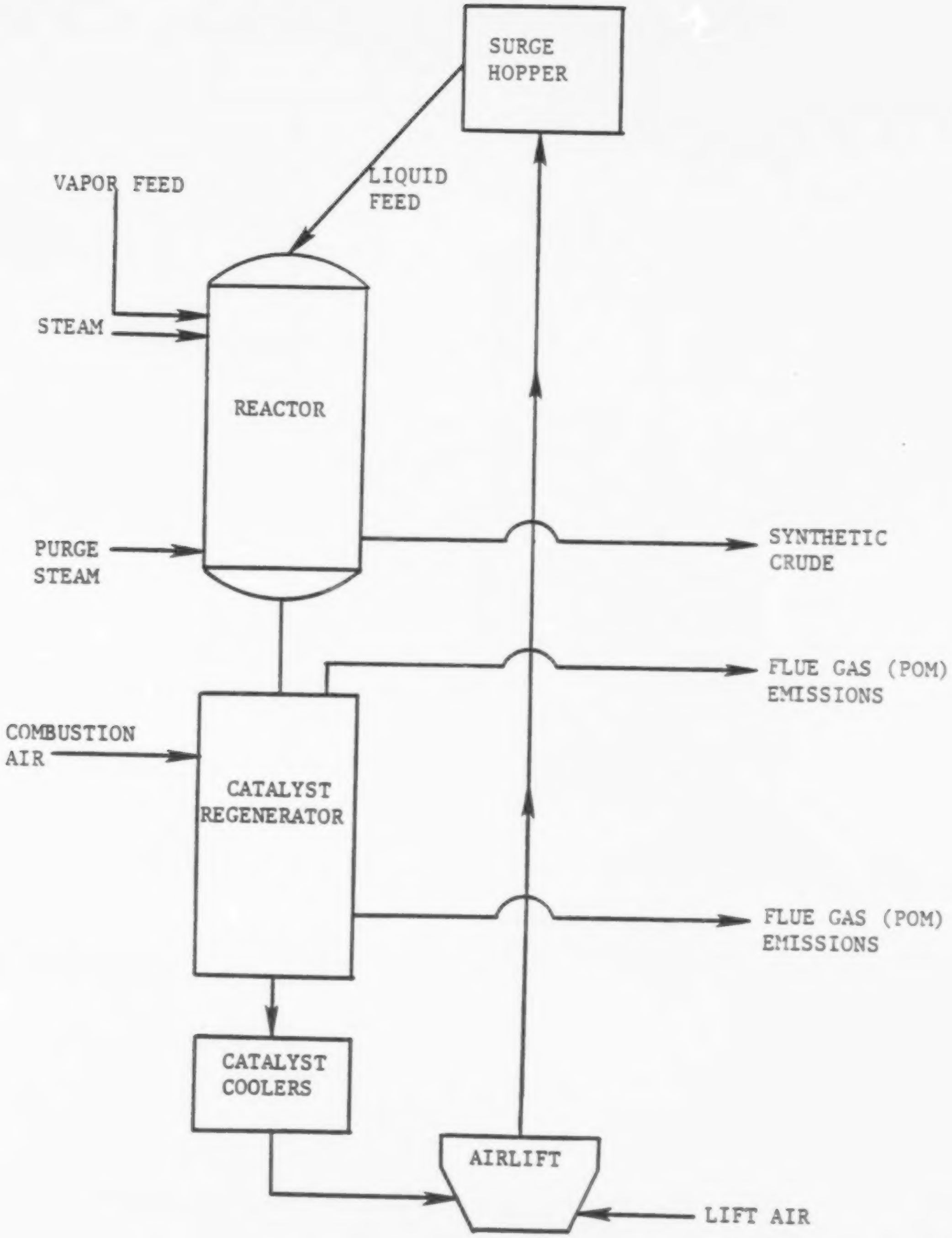

SURGE HOPPER
VAPOR FEED
LIQUID FEED
STEAM
REACTOR
PURGE STEAM
SYNTHETIC CRUDE
FLUE GAS (POM) EMISSIONS
COMBUSTION AIR
CATALYST REGENERATOR
FLUE GAS (POM) EMISSIONS
CATALYST COOLERS
AIRLIFT
LIFT AIR

Figure 11. Diagram of a Thermofar catalytic cracking process.[97]

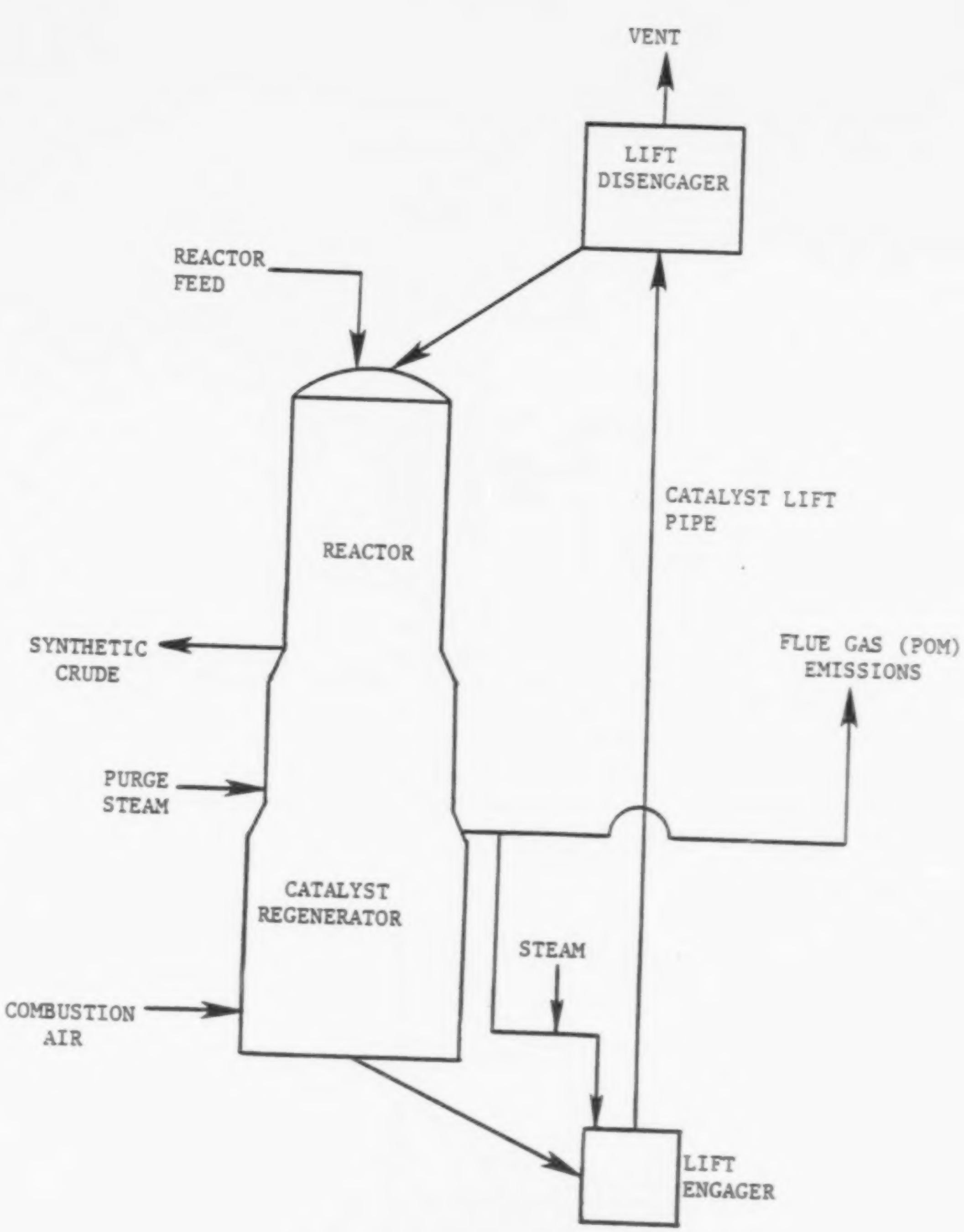

VENT
LIFT DISENGAGER
REACTOR FEED
CATALYST LIFT PIPE
REACTOR
SYNTHETIC CRUDE
FLUE GAS (POM) EMISSIONS
PURGE STEAM
CATALYST REGENERATOR
STEAM
COMBUSTION AIR
LIFT ENGAGER

Figure 12. Diagram of a Houdriflow catalytic cracking process.[97]

Another means of reducing potential POM emissions from the catalyst regenerators would be to achieve more complete combustion of carbon monoxide to carbon dioxide. Recently developed processes such as UOP^{R} hot regeneration and Amoco Ultracat^{R} may aid in the achievement of lower overall POM emissions. The relatively higher temperatures for catalyst regeneration used in the UOP process serve to improve coke combustion efficiency and thus potentially reduce POM formation and emissions. One drawback to the UOP process is that due to its higher temperatures, special materials of construction are required, thus making it more suitable for new cracking units as opposed to existing units. The Amoco process, however, is based on improving the catalytic reactor efficiency and allowing more complete combustion to occur in the catalyst regenerator without having to operate at higher temperatures. Because changes in basic equipment are minimal with the Amoco process, it is more amenable for retrofitting existing units.[95]

Emission Factors

Available emission factor data for catalyst regenerators used in FCC, TCC, and HCC units are presented in Table 42.[97] Factors for all three types of units generally exhibit a large amount of variability. In uncontrolled FCC units, pyrene, phenanthrene, and fluoranthene were the predominant compounds measured. Perylene, anthracene, and coronene were not detected in uncontrolled emissions from the FCC unit. Benzo(a)pyrene levels were found to be relatively minor (average of 169 ug/barrel of oil feed versus average of 133,000 ug/barrel of oil feed for phenanthrene). The positive effect of carbon monoxide waste heat boilers as control devices for FCC regenerator flue gases is well evidenced in Table 42.[97]

Polycyclic organic matter emissions were in general highest from the controlled TCC unit (air lift type) and the uncontrolled HCC unit. In the air lift TCC unit, pyrene, phenanthrene, benzo(g,h,i)perylene, and benzo(a)pyrene emission levels were the highest of the ten POMs measured. Similarly, benzo(g,h,i)perylene, benzo(e)pyrene, pyrene, and benzo(a)pyrene were the most significant compounds measured in uncontrolled HCC unit

TABLE 42. POM EMISSION FACTORS FOR PETROLEUM CAT

Unit Type	Emission Point	Number of Tests	Benzo(a)pyrene	Pyrene	Benzo(e)pyrene
FCC	Uncontrolled Regenerator Outlet	3	4.3 - 460 Avg. 169	40 - 28,000 Avg. 9,402	11 - 3,600 Avg. 1,221
FCC	CO Waste Heat Boiler Outlet	3	ND - 21.5 Avg. 11	25 - 165 Avg. 92	ND - 21 Avg. 13
TCC (air lift)	Controlled Regenerator Outlets[c]	3	56,000 - 120,000 Avg. 79,333	132,000 - 260,000 Avg. 214,000	56,000 - 120,00 Avg. 47,667
TCC (bucket lift)	Controlled Regenerator Outlets[c]	2	ND - 31 Avg. 16	280 - 360 Avg. 320	ND - 82 Avg. 41
HCC	Uncontrolled Regenerator Outlet	2	205,000 - 231,000 Avg. 218,000	130,000 - 131,000 Avg. 130,500	310,000 - 380,0 Avg. 345,000
HCC	CO Waste Heat	1	45	39	97

---

[a] These ten POM compounds were all that were analyzed for in Reference 97. They do not, therefore, necessarily represent all the POM compounds present in emissions from this source category.

[b] Emission factor values were measured using techniques that collected particulate and vaporized POM.

[c] Emissions were vented through plume burners prior to being emitted from the regenerators.

[d] ND in all cases means compound was not detected. Lower limit of detection was not specified in Reference 97.

TROLEUM CATALYTIC CRACKING CATALYST REGENERATION UNITS[97]

POM Emission Factors, µg/Barrel Oil Charged (Fresh Feed and Recycle)[a,b]							
Benzo(e)pyrene	Perylene	Benzo(g,h,i)-perylene	Anthanthrene	Coronene	Anthracene	Phenanthrene	Fluoranthene
11 - 3,600 Avg. 1,221	ND[d]	ND - 424 Avg. 146	ND	ND	ND - 2,070 Avg. 690	ND - 400,000 Avg. 133,333	44 - 20,000 Avg. 6,735
ND - 21 Avg. 13	ND	ND - 55 Avg. 18	ND	ND	ND	ND	20 - 85 Avg. 59
56,000 - 120,000 Avg. 47,667	5,500 - 10,000 Avg. 8,100	44,000 - 72,000 Avg. 56,667	1,300 - 4,400 Avg. 2,483	ND - 360 Avg. 120	10,300 - 24,000 Avg. 14,967	78,000 - 352,000 Avg. 253,333	ND - 29,000 Avg. 13,200
ND - 82 Avg. 41	ND	ND	ND	ND	ND	ND	59 - 106 Avg. 83
310,000 - 380,000 Avg. 345,000	Both at 34,000 Avg. 34,000	300,000 - 380,000 Avg. 340,000	15,000 - 18,000 Avg. 16,500	11,200 - 26,000 Avg. 18,600	920 - 2,000 Avg. 1,460	21,000 - 29,000 Avg. 25,000	8,300 - 11,400 Avg. 9,850
97	4.8	125	3.2	8.0	7.9	83	23

e POM compounds

emissions. No explanation was offered in Reference 97 of why POM emissions from the controlled bucket lift TCC unit were so disproportionately less than that from the air lift TCC unit. Both types of TCC units were equipped with plume burners.

The data for the HCC unit reinforces the effectiveness of venting regenerator emissions to carbon monoxide waste heat boilers for POM emission control. For each of the ten POM compounds measured, the waste heat boiler reduced uncontrolled HCC regenerator emissions by greater than 99 percent.

Source Locations

Locations of catalytic crackers and their catalyst regenerators are directly associated with the locations of petroleum refineries. As of January 1, 1986, there were a total of 189 operating refineries in the United States. The States of Texas, California, and Louisiana contain about 41 percent of the total. Not all of the 189 refineries, however, contain catalytic crackers. A list of the refineries containing catalytic crackers and that may be potential POM emission sources is given in Table 43.[98]

SINTERING IN THE IRON AND STEEL INDUSTRY

Process Description

In the iron and steel industry, sintering processes convert materials such as fine iron ore concentrates, blast furnace flue dust, mill scale, turnings, coke fines, and limestone fines into an agglomerated product that is suitable for use as blast furnace feed material. Sintering is necessary because fine iron ore material, whether in natural or concentrated ores, must be aggregated to a size and strength to prevent it from being blown out of the top of a blast furnace.[99,100] A typical sintering operation is illustrated in Figure 13.[101]

TABLE 43. LOCATIONS OF ACTIVE PETROLEUM REFINERIES WITH CATALYTIC CRACKERS AS OF JANUARY 1986[98]

Company	Location
Lion Oil Company	El Dorado, AR
Atlantic Richfield Company	Carson, CA
Champlin Petroleum Company	Wilmington, CA
Chevron U.S.A., Inc.	El Segundo, CA Richmond, CA
Exxon Company	Benicia, CA
Fletcher Oil and Refinery Company	Carson, CA
Golden West Refining Company	Santa Fe Springs, CA
Mobil Oil Corporation	Torrance, CA
Shell Oil Company	Martinez, CA Wilmington, CA
Superior Processing Company	Santa Fe Springs, CA
Texaco Refining and Marketing, Inc.	Wilmington, CA
Tosco Corporation	Martinez, CA
Union Oil of California	Los Angeles, CA
Asamera Oil U.S., Inc.	Commerce City, CO
Conoco, Inc.	Commerce City, CO
Texaco Refining and Marketing, Inc.	Delaware City, DE
Chevron U.S.A., Inc.	Barber's Point, HA
Clark Oil and Refining Corporation	Blue Island, IL Hartford, IL
Marathon Oil Company	Robinson, IL
Mobil Oil Corporation	Joliet, IL
Shell Oil Company	Wood River, IL
Texaco Refining and Marketing, Inc.	Lawrenceville, IL
Union Oil of California	Lemont, IL
Amoco Oil Company	Whiting, IN
Indiana Farm Bureau Cooperative Association, Inc.	Mt. Vernon, IN

TABLE 43. LOCATIONS OF ACTIVE PETROLEUM REFINERIES WITH CATALYTIC CRACKERS AS OF JANUARY 1986[98] (Continued)

Company	Location
Rock Island Refining Corporation	Indianapolis, IN
Derby Refining Company	Wichita, KS
Farmland Industries, Inc.	Coffeyville, KS
National Cooperative Refinery Association	McPherson, KS
Pester Refining Company	El Dorado, KS
Texaco Refining and Marketing, Inc.	El Dorado, KS
Total Petroleum, Inc.	Arkansas City, KS
Ashland Petroleum Company	Catlettsburg, KY
BP Oil, Inc.	Belle Chasse, LA
Citgo Petroleum Corporation	Lake Charles, LA
Conoco, Inc.	Lake Charles, LA
Exxon Company	Baton Rouge, LA
Gulf Products Company	Belle Chasse, LA
Hill Petroleum Company	Krotz Springs, LA
Marathon Oil Company	Garyville, LA
Murphy Oil U.S.A., Inc.	Meraux, LA
Placid Refining Company	Port Allen, LA
Shell Oil Company	Norco, LA
Tenneco Oil Company	Chalmette, LA
Texaco Refining and Marketing, Inc.	Convent, LA
Marathon Oil Company	Detroit, MI
Total Petroleum, Inc.	Alma, MI
Ashland Petroleum Company	St. Paul Park, MN
Koch Refining Company	Rosemount, MN
Amerada-Hess Corporation	Purvis, MS
Chevron U.S.A., Inc.	Pascagoula, MS
Ergon Refining, Inc.	Vicksburg, MS
Cenex	Laurel, MT

TABLE 43. LOCATIONS OF ACTIVE PETROLEUM REFINERIES WITH CATALYTIC CRACKERS AS OF JANUARY 1986[98] (Continued)

Company	Location
Conoco, Inc.	Billings, MT
Exxon Company	Billings, MT
Montana Refining Company	Great Falls, MT
Amerada-Hess Corporation	Port Reading, NJ
Coastal Eagle Point Oil Company	Westville, NJ
Exxon Company	Linden, NJ
Mobil Oil Corporation	Paulsboro, NJ
Texaco Refining and Marketing, Inc.	Westville, NJ
Bloomfield Refining Company	Bloomfield, NM
Giant Industries, Inc.	Gallup, NM
Navajo Refining Company	Artesia, NM
Amoco Oil Company	Mandan, ND
Ashland Petroleum Company	Canton, OH
Chevron U.S.A., Inc.	Cincinnati, OH
Standard Oil Company of Ohio	Lima, OH Toledo, OH
Sun Cl	Toledo, OH
Conoco, Inc.	Ponca City, OK
Kerr-McGee Refining Corporation	Wynnewood, OK
Sinclair Oil Corporation	Tulsa, OK
Sun Cl	Tulsa, OK
Total Petroleum, Inc.	Ardmore, OK
Atlantic Richfield Company	Philadelphia, PA
BP Oil Corporation	Marcus Hook, PA
Chevron U.S.A., Inc.	Philadelphia, PA
Sun Cl	Marcus Hook, PA
United Refining Company	Warner, PA
Mapco Petroleum, Inc.	Memphis, TN
Amber Refining Company	Fort Worth, TX

TABLE 43. LOCATIONS OF ACTIVE PETROLEUM REFINERIES WITH CATALYTIC CRACKERS AS OF JANUARY 1986[98] (Continued)

Company	Location
American Petrofina, Inc.	Port Arthur, TX
Amoco Oil Company	Texas City, TX
Atlantic Richfield Company	Houston, TX
Champlin Petroleum Company	Corpus Christi, TX
Charter International Oil Company	Houston, TX
Chevron U.S.A., Inc.	El Paso, TX
	Port Arthur, TX
Coastal States Petroleum Company	Corpus Christi, TX
Fina Oil and Chemical	Big Spring, TX
Crown Central Petroleum Corporation	Houston, TX
Diamond Shamrock Corporation	Sunray, TX
	Three Rivers, TX
Exxon Company	Baytown, TX
Koch Refining Company	Corpus Christi, TX
LaGloria Oil and Gas Company	Tyler, TX
Marathon Petroleum Company	Texas City, TX
Mobil Oil Corporation	Beaumont, TX
Phillips 66 Company	Borger, TX
	Sweeny, TX
Shell Oil Company	Deer Park, TX
	Odessa, TX
Southwestern Refining Cl	Corpus Christi, TX
Texaco Refining and Marketing, Inc.	Port Neches, TX
	El Paso, TX
	Port Arthur, TX
Texas City Refining, Inc.	Texas City, TX
Union Oil Company of California	Nederland, TX
Valero Refining Company	Corpus Christi, TX
Amoco Oil Company	Salt Lake City, UT
Big West Oil Company	Salt Lake City, UT

TABLE 43. LOCATIONS OF ACTIVE PETROLEUM REFINERIES WITH CATALYTIC CRACKERS AS OF JANUARY 1986[98] (Continued)

Company	Location
Chevron U.S.A., Inc.	Salt Lake City, UT
Phillips 66 Company	Woods Cross, UT
RMT Properties, Inc.	Salt Lake City, UT
Seagull Refining Company	Roosevelt, UT
Amoco Oil Company	Yorktown, VA
Mobil Oil Corporation	Ferndale, WA
Shell Oil Company	Anacortes, WA
Texaco Refining and Marketing, Inc.	Anacortes, WA
Murphy Oil U.S.A., Inc.	Superior, WI
Amoco Oil Company	Casper, WY
Big West Oil Company	Cheyenne, WY
Little American Refining Company	Casper, WY
Sinclair Oil Corporation	Sinclair, WY
Wyoming Refining Company	New Castle, WY

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

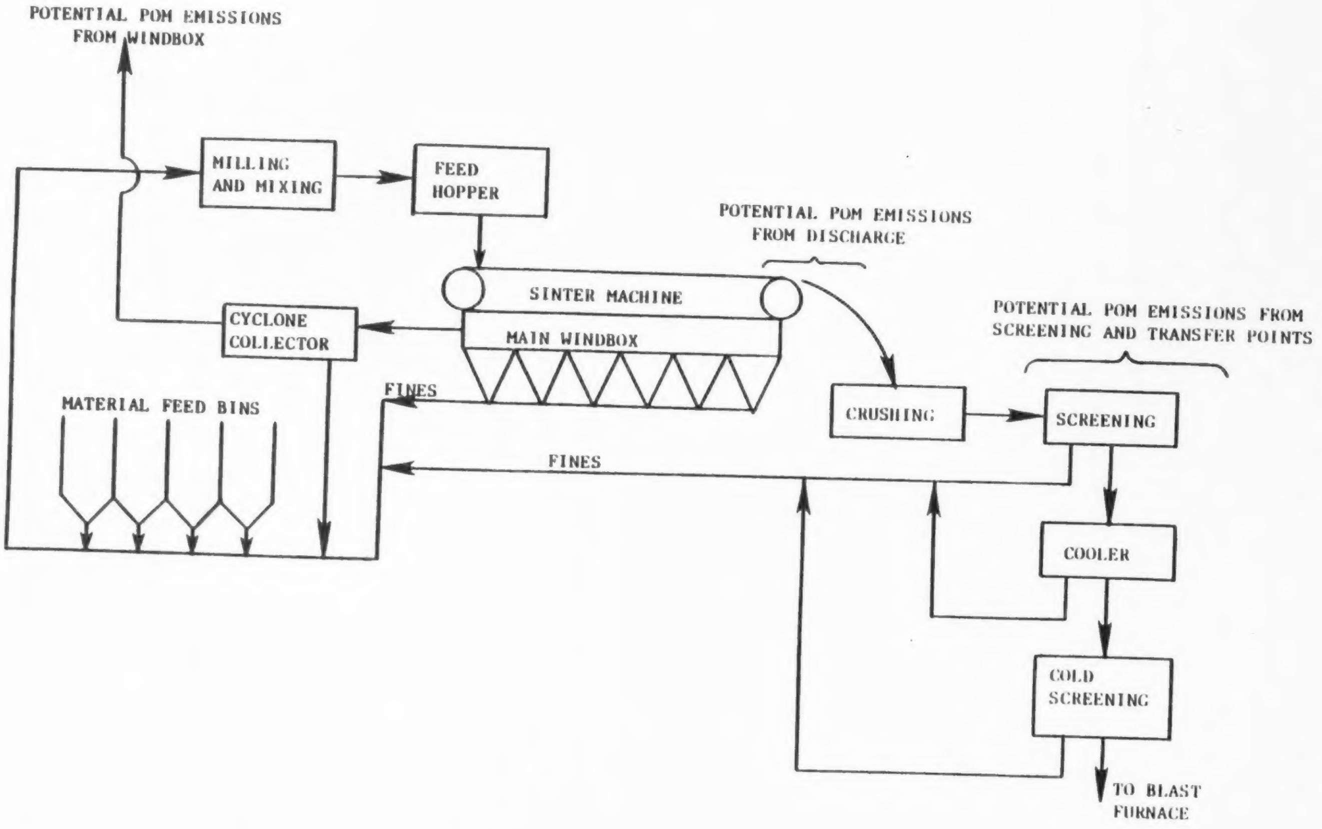

POTENTIAL POM EMISSIONS FROM WINDBOX
MILLING AND MIXING
FEED HOPPER
POTENTIAL POM EMISSIONS FROM DISCHARGE
SINTER MACHINE
CYCLONE COLLECTOR
MAIN WINDBOX
POTENTIAL POM EMISSIONS FROM SCREENING AND TRANSFER POINTS
MATERIAL FEED BINS
FINES
CRUSHING
SCREENING
FINES
COOLER
COLD SCREENING
TO BLAST FURNACE

Figure 13. Configuration of a typical sintering facility.[101]

Sintering begins by mixing iron-bearing materials with coke or coal fines, limestone fines (a flux material), water, and other recycled dusts (e.g., blast furnace flue dust) to obtain the desired sinter feed composition. The prepared feed is distributed evenly onto one end of a continuous traveling grate or strand. After the feed has been deposited on the strand, the coke on the mixture is ignited by a gas- or oil-fired furnace. After the coke has been ignited, the traveling strand passes over windboxes where an induced downdraft maintains combustion in the sinter bed. This combustion creates sufficient temperatures [1300 to 1500°C (2400 to 2700°F)] to fuse the metal particles into a porous clinker that can be used as blast furnace feed.[99,100]

Once the sintering process is completed, the sintered material is discharged from the sinter strand into a crushing operation. Following crushing, the broken sinter falls onto sizing screens where undersized material is collected and recycled to the start of the sintering process. The oversized sinter clinker is then sent to a cooling process. The most common types of sinter coolers used include circular or straight line moving beds, quiescent beds, or shafts. Air or water is used as the cooling medium in these coolers, with air being prevalent in newer plants and water being dominant is older plants. The cooled sinter is either sent directly to a blast furnace, sent to storage, or screened again, prior to blast furnace usage, to obtain a more precise size specification.[99,100]

Polycyclic organic matter emissions originate in the sintering process from the burning of coke and potentially oily materials in the sinter feed. Potentially, POM emissions may be released from the sinter machine windbox, from the sinter machine discharge point, and from sinter product processing operations (i.e., crushing, screening, and cooling). Because of the high temperatures used in sintering operations, it is probable that sinter plant POM emissions are in both gaseous and particulate matter forms.[99,102]

Emissions control at sintering facilities typically involves emissions collection and conveyance to a standard particulate control device such as a baghouse, ESP, or wet scrubber. If substantial quantities of POM emissions are in gaseous form, wet scrubbers would likely be the most efficient in reducing total POM because gaseous compounds would be condensed in the scrubber.[99-102]

Emission Factors

Only one emission factor for POM compounds from sintering operations is available from the literature. Emissions of benzo(a)pyrene have been determined to range from 600 ug/Mg to 1.1 g/Mg of sinter feed processed. The precise source of the emissions (windbox, discharge point, etc.) and the control status of the source are not defined in the literature. Available data do not indicate whether the range of 600 ug/Mg to 1.1 g/Mg represents only particulate benzo(a)pyrene or particulate and gaseous benzo(a)pyrene.[102]

Source Locations

Iron and steel sintering facilities are located in conjunction with the operation of iron and steel blast furnaces. The largest concentration of sintering processes in the United States is in the steel producing regions of Ohio, Pennsylvania, and Indiana. The American Iron and Steel Institute indicated that no current central, organized list of sintering facilities was available. Locations of sinter facilities according to a preliminary survey in 1977 by the U. S. EPA are identified in Table 44.[101]

FERROALLOY MANUFACTURING

Process Description

Ferroalloys are crude alloys of iron and one or more other elements which are used for deoxidizing molten steels and making alloy steels. The major types of ferroalloys produced are listed in Table 45.[103] Ferroalloys can be produced by five different processes, the primary method of production being the use of electric arc furnaces (EAF). Emissions of POM compounds are possible from ferroalloy manufacturing because coke or coal is

TABLE 44. LOCATIONS OF IRON AND STEEL INDUSTRY SINTER PLANTS IN 1977[101]

Company	Plant Location
Republic Steel Corporation	Gadsden, AL
U. S. Steel Corporation	Bessemer, AL
Kaiser Steel Corporation	Fontana, CA
C. F. & I. Steel Corporation	Pueblo, CO
Interlake Steel Corporation	South Chicago, IL
Calumet Steel Division	Chicago Heights, IL
Republic Steel Corporation	Chicago, IL
U. S. Steel Corporation	South Chicago, IL
Granite City Steel Division	Granite City, IL
Wisconsin Steel Division	South Chicago, IL
Inland Steel Corporation	East Chicago, IL
U. S. Steel Corporation	Gary, IN
Youngstown Sheet and Tube	East Chicago, IN
Bethlehem Steel Corporation	Burns Harbor, IN
Armco Steel Corporation	Ashland, KY
Bethlehem Steel Corporation	Sparrows Point, MD
National Steel Corporation	Detroit, MI
Great Lakes Steel Company	River Rouge, MI
Bethlehem Steel Corporation	Buffalo, NY
Jones and Laughlin Steel	Star Lake, NY
Republic Steel Corporation	Cleveland, OH
Jones and Laughlin Steel	Cleveland, OH
U. S. Steel Corporation	Lorain, OH
Republic Steel Corporation	Youngstown, OH
U. S. Steel Corporation	Youngstown, OH
Youngstown Sheet and Tube	Campbell, OH
Republic Steel Corporation	Warren, OH
U. S. Steel Corporation	Fairless Hills, PA

TABLE 44. LOCATIONS OF IRON AND STEEL INDUSTRY SINTER PLANTS IN 1977[101] (Continued)

Company	Plant Location
U. S. Steel Corporation	Braddock, PA
U. S. Steel Corporation	Saxonburg, PA
U. S. Steel Corporation	Homestead, PA
Jones and Laughlin Steel	Aliquippa, PA
U. S. Steel Corporation	Rankin, PA
Bethlehem Steel Corporation	Johnstown, PA
U. S. Steel Corporation	McKeesport, PA
Alan Wood Steel	Swedeland, PA
Bethlehem Steel Corporation	Bethlehem, PA
Wheeling-Pittsburgh Steel	Monessen, PA
Bethlehem Mines Corporation	Morgantown, PA
Armco Steel Corporation	Houston, TX
Lone Star Steel Company	Lone Star, TX
U. S. Steel Corporation	Provo, UT
Wheeling-Pittsburgh Steel	Follansbee, WV
Weirton Steel Company	Weirton, WV

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

TABLE 45. MAJOR TYPES OF FERROALLOYS PRODUCED IN THE UNITED STATES[103]

Silvery Iron
50 percent Ferrosilicon
65 to 75 percent Ferrosilicon
Silicon Metal
Calcium Silicon
Silicomanganese Zirconium
High-carbon Ferromanganese
Silicomanganese
Ferromanganese Silicon
Charge Chrome and High-carbon Ferrochrome
Ferrochrome Silicon
Calcium Carbide
Low-carbon Ferrochrome
Low-carbon Ferromanganese
Medium-carbon Ferromanganese
Chromium Metal
Manganese Metal
Ferrotitanium
Ferrovanadium
Ferromolybdenum

charged to the high temperature smelting furnaces used in the ferroalloy industry and burned. Because combustion efficiency in the furnace environment is low, unburned hydrocarbons, including several POM compounds, are formed and emitted with the furnace exhaust. Ferroalloy production processes other than EAFs have not been identified as POM emission sources.[99]

The electric arc furnace method of ferroalloy production is depicted in Figure 14.[103,104] Metal ores and other necessary raw materials such as quartz or quartzite (slagging materials), alumina (a reducing agent), limestone, coke or coal, and steel scrap are brought to ferroalloy facilities by ship, truck, or rail and stored on-site. Depending on its moisture content and physical configuration, metal ore may need to be dried and/or sintered prior to being crushed, sized, and mixed with other process raw materials. Once the proper charge mixture has been prepared, the charge is weighed and fed to a submerged EAF for smelting.

Three types of EAFs can be used for ferroalloy production. These three, open, sealed, and semisealed, may be charged continuously or intermittently. Electric arc furnaces contain three carbon electrodes which are vertically suspended above the furnace hearth and extend 1 to 1.5 m (3 to 5 ft) into the charge materials. Three-phase current arcs through the charge materials from electrode to electrode, and the charge is smelted as electrical energy is converted to heat. The intense heat around the electrodes [2204-2760°C (4000-5000°F)] results in carbon reduction of the metal (e.g., chrome, manganese) and iron oxides in the charge and the formation of the particular ferroalloy. The molten ferroalloy is periodically tapped into ladles from tapholes in the lower furnace wall.[103-105]

The molten ferroalloy is cast into molds and allowed to cool and solidify. The casts are then removed from the molds, graded, and broken. The broken ferroalloy is passed through a crusher and screened. The ferroalloy product is then stored, packaged, and shipped to the consumer.

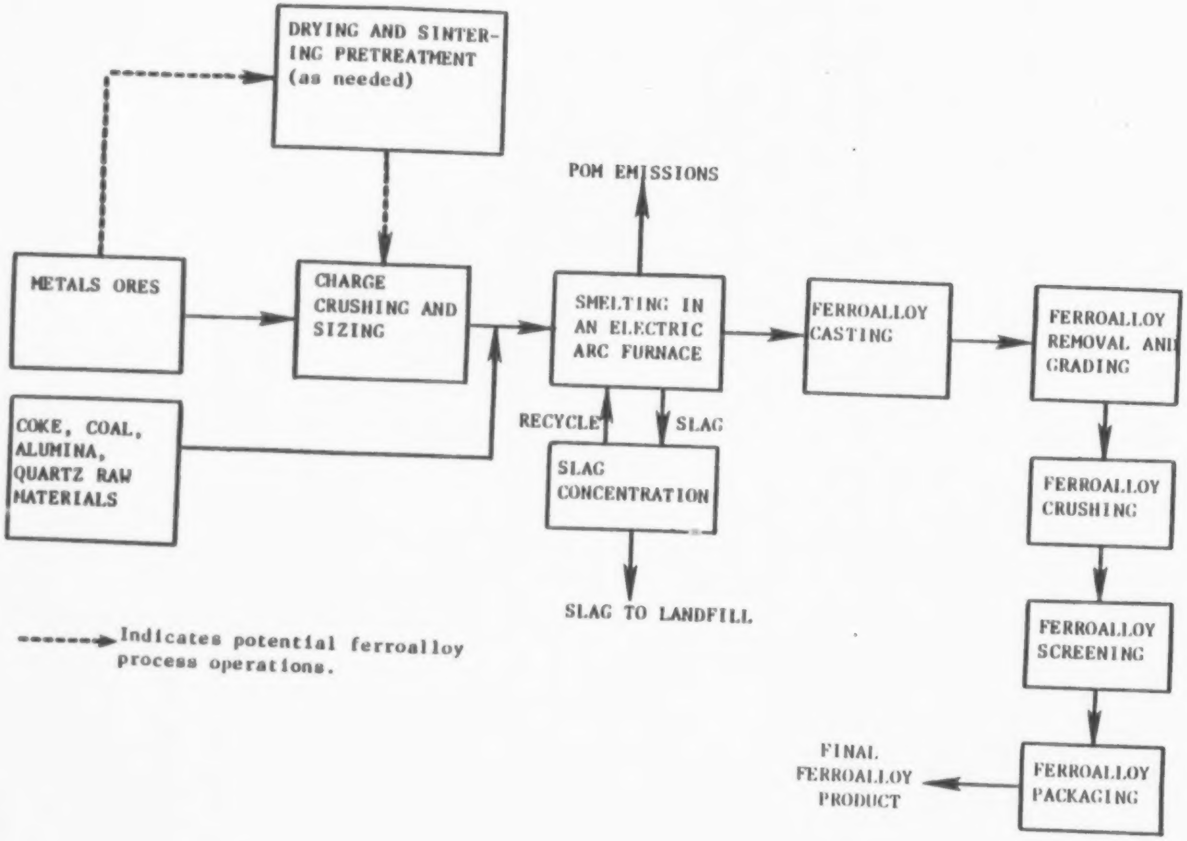

DRYING AND SINTERING PRETREATMENT (as needed)
METALS ORES
CHARGE CRUSHING AND SIZING
COKE, COAL, ALUMINA, QUARTZ RAW MATERIALS
POM EMISSIONS
SMELTING IN AN ELECTRIC ARC FURNACE
RECYCLE
SLAG
SLAG CONCENTRATION
SLAG TO LANDFILL
FERROALLOY CASTING
FERROALLOY REMOVAL AND GRADING
FERROALLOY CRUSHING
FERROALLOY SCREENING
FERROALLOY PACKAGING
FINAL FERROALLOY PRODUCT
Indicates potential ferroalloy process operations.

Figure 14. Typical electric arc furnace ferroalloy manufacturing process.[103]

Impurities from the smelting process are trapped in a slag which forms inside the electric arc furnace. The slag is periodically tapped and treated by a concentration process to recovery metal values. Slag is processed in a flotation system, where metal particles sink to the bottom while slag floats. The recovered metals are recycled to the furnace, and the remaining slag is removed and disposed of.

Of the three types of EAFs that may be used to produce ferroalloys, open furnaces are the most common type, and also have the highest potential for particulate emissions. An open furnace is pictured in Figure 15.[104] A hood is usually located 1.8 to 2.4 m (6 to 8 ft) above the furnace crucible rim. Dust and fumes from the smelting process are drawn into the hood along with large volumes of ambient air. Advantages of the open furnace include the ability to stoke it during operation and the flexibility to manufacture several types of ferroalloy without altering the furnace design.[103-105]

The semisealed (or semi-enclosed) furnace is pictured in Figure 16.[104] A cover seals the top of the furnace except for openings around the electrodes through which raw material is charged. These furnaces are either hooded or maintained under negative pressure to collect emissions from around the electrodes. Because semisealed furnaces cannot be stoked, crusting and bridging of ferroalloys around the electrodes and charge holes may prevent uniform descent of the charge into the furnace and blows (jets of extremely hot gases originating in the high temperature zone near the electrode tips) may emerge around the electrodes at high velocity.[103-105]

The third type of EAF, the sealed or closed furnace, is illustrated in Figure 17.[104] Packing is used to seal the cover around the electrodes and charging chutes. The furnace is not stoked and a slight positive pressure is maintained to prevent leakage of the air into the furnace. Care must also be taken to prevent water leaks which may cause explosive gas release which could damage the furnace and threaten worker safety. Sealed furnace designs are specifically used in the manufacture of narrow families of ferroalloys, so plants using sealed furnaces have less flexibility to produce different types of ferroalloys.

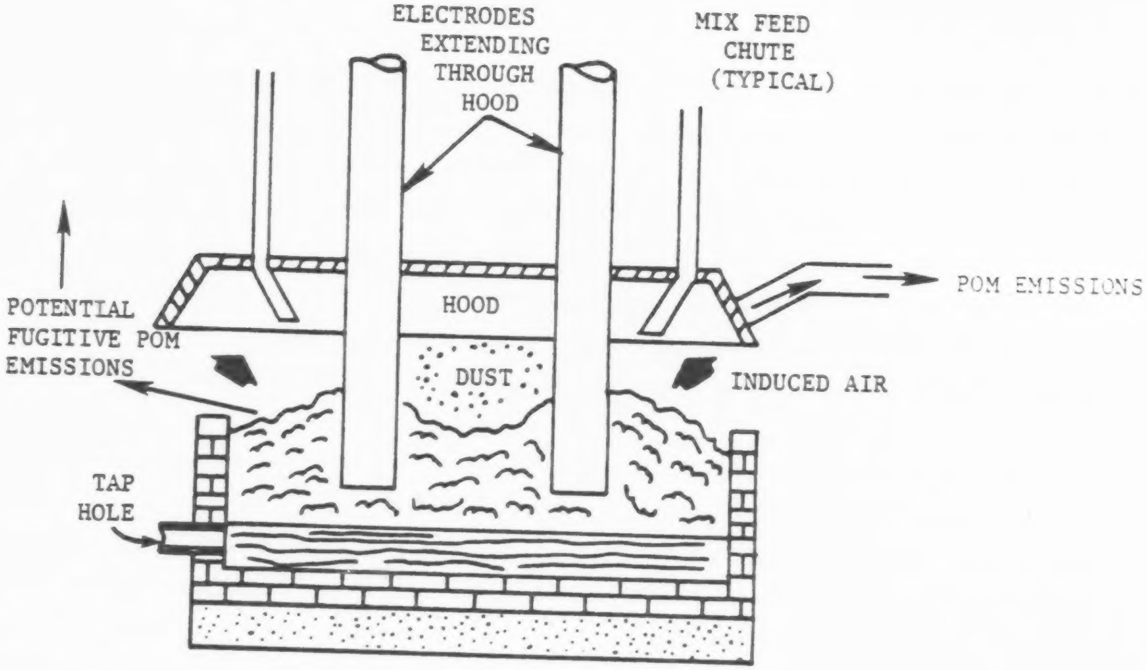

ELECTRODES EXTENDING THROUGH HOOD
MIX FEED CHUTE (TYPICAL)
POM EMISSIONS
HOOD
POTENTIAL FUGITIVE POM EMISSIONS
DUST
INDUCED AIR
TAP HOLE

Figure 15. Open electric arc furnace.[104]

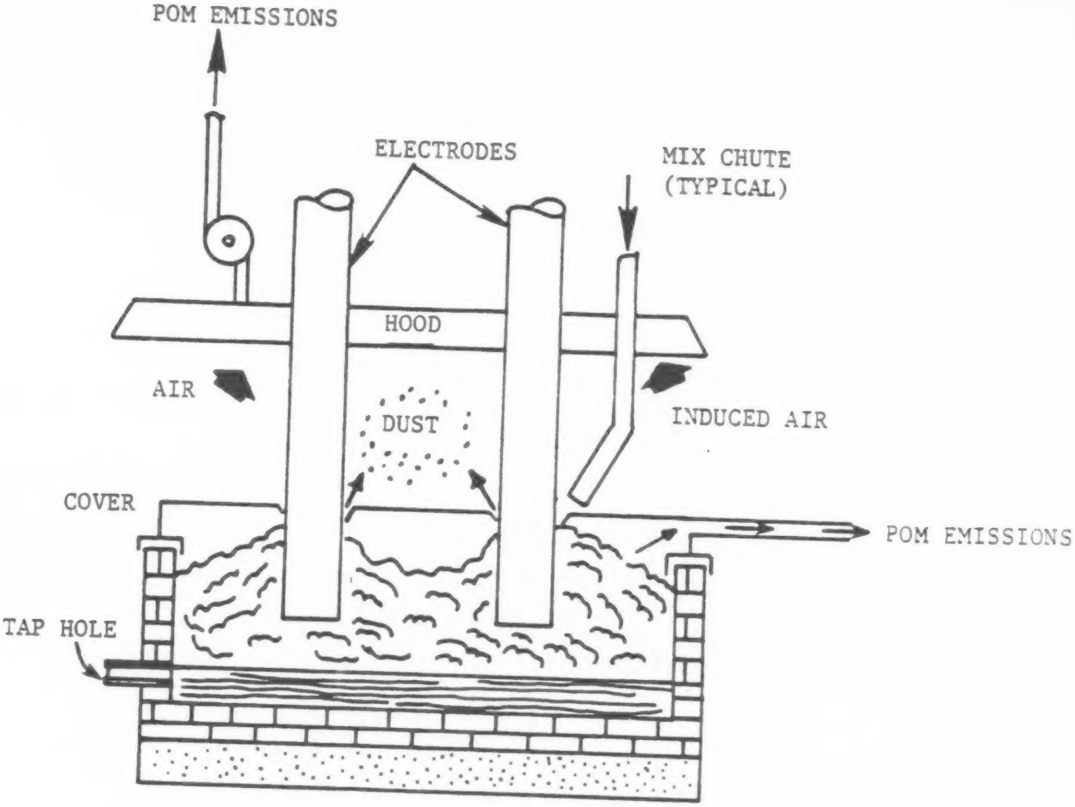

POM EMISSIONS
ELECTRODES
MIX CHUTE (TYPICAL)
HOOD
AIR
DUST
INDUCED AIR
COVER
POM EMISSIONS
TAP HOLE

Figure 16. Semisealed electric arc furnace.[104]

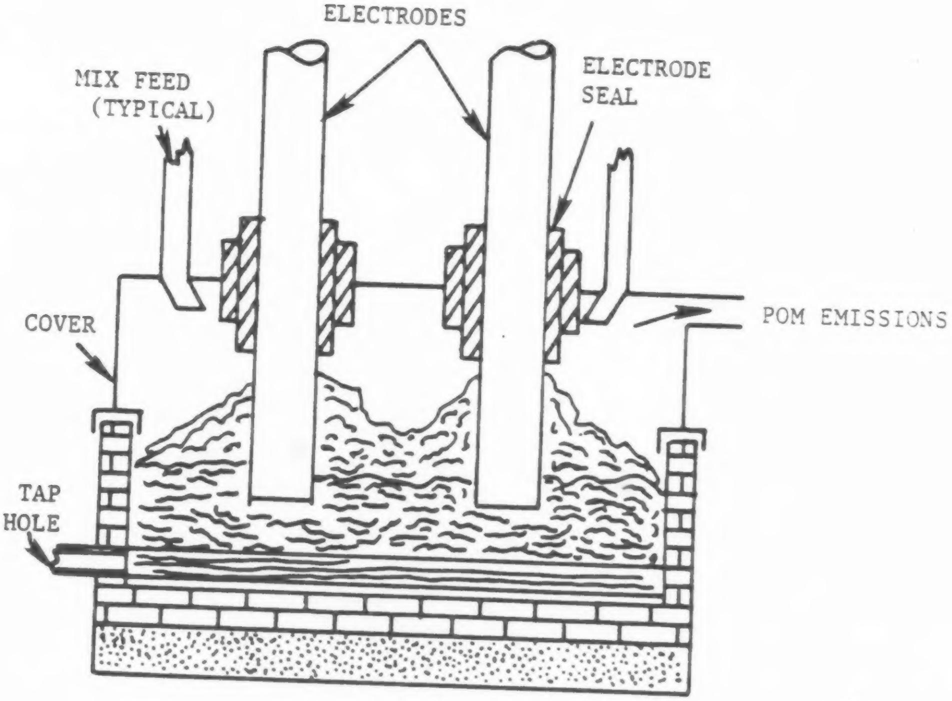

ELECTRODES
MIX FEED (TYPICAL)
ELECTRODE SEAL
COVER
POM EMISSIONS
TAP HOLE

Figure 17. Sealed electric arc furnace.[104]

One alternative to the electric arc furnace process which can be used to produce some low-carbon ferroalloys is a type of exothermic process involving silicon reduction. A flow diagram of the process for chromium ferroalloys is shown in Figure 18.[104,105] First, chromium ore and lime are fused together in a furnace to produce a chrome ore/lime melt which is poured into a reaction ladle (number 1). Then a known quantity of molten ferrochrome silicon previously produced in another reaction ladle (number 2) is added to ladle 1. In the ladle, a rapid, heat-producing reaction results in the reduction of the chromium from its oxide form and the formation of low-carbon ferrochrome and a calcium silicate slag. The ferrochrome product is then cooled, finished, and packaged. Since the slag from ladle 1 still contains recoverable chromium oxide, it is reacted in ladle 2 with molten ferrochrome-silicon produced in a submerged arc furnace. The exothermic reaction in ladle 2 produces the ferrochrome-silicon added to the number 1 ladle during the next production cycle.

A vacuum furnace process can also be used to produce low-carbon ferrochrome ferroalloys. This type of furnace, pictured in Figure 19, is charged with high-carbon ferrochrome and heated to a temperature near the melting point of the alloy. Decarburization occurs as the high-carbon ferrochrome is oxidized by the silica oxide in the ferrochrome. Carbon monoxide gas resulting from the reaction is pumped out of the furnace to maintain a high vacuum and promote decarburization of the ferrochrome.[104,105]

The electrolytic process is another alternative to the electric arc furnace for producing chromium and manganese ferroalloys. Pure chromium and manganese metal is generally produced this way. Chromite or manganese ore, high-chromic or high-manganese oxide slags, or ferrochrome or ferromanganese can be used as raw materials for the process. Preparation of raw materials can include grinding, calcining, and leaching. In the electrolytic process, metal ions contained in an electrolytic solution are plated on cathodes by a low voltage direct current. The pure metal forms a film on the cathode about 0.3 cm (1/8 in) thick, which is removed and prepared for shipment.[104,105]

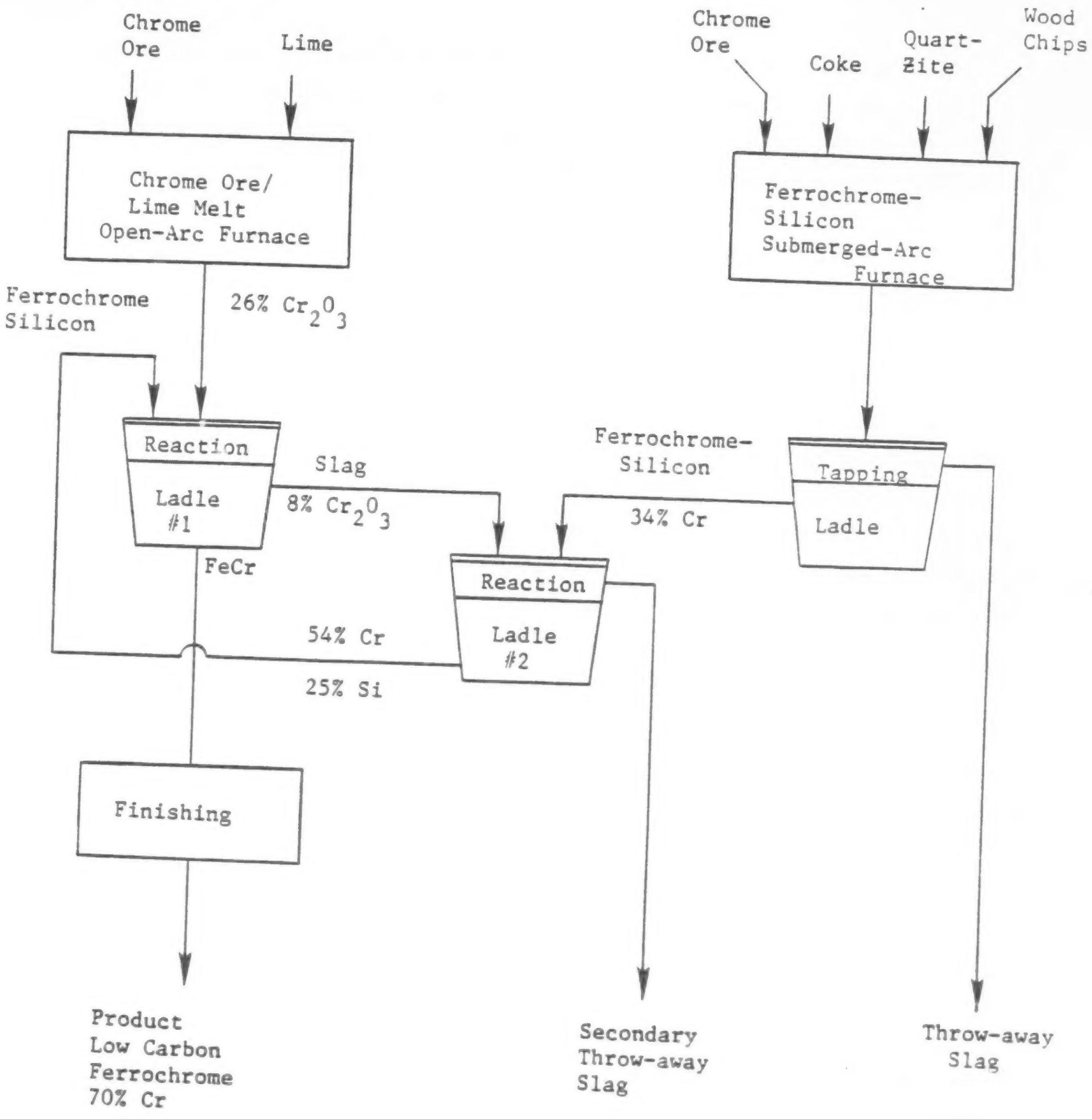

Chrome Ore
Lime
Chrome Ore/ Lime Melt Open-Arc Furnace
Chrome Ore
Coke
Quartzite
Wood Chips
Ferrochrome-Silicon Submerged-Arc Furnace
Ferrochrome Silicon
26% Cr_2O_3
Reaction
Ladle #1
Slag
8% Cr_2O_3
Ferrochrome-Silicon
34% Cr
Tapping
Ladle
FeCr
Reaction
Ladle #2
54% Cr
25% Si
Finishing
Product Low Carbon Ferrochrome 70% Cr
Secondary Throw-away Slag
Throw-away Slag

Figure 18. Typical flow chart for the production of low-carbon ferrochrome by the exothermic silicon reduction process.105

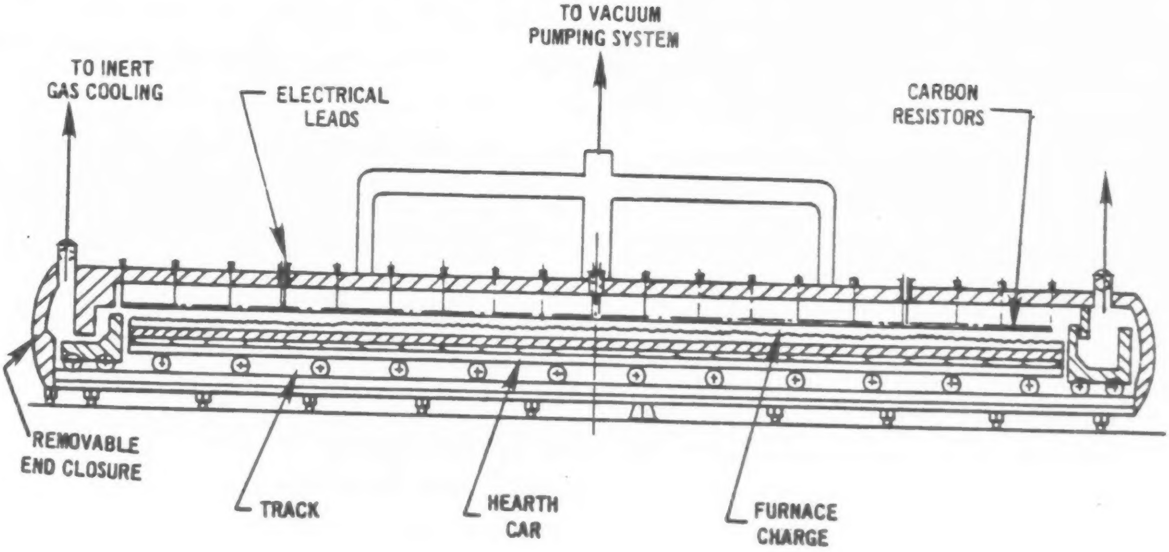

TO VACUUM PUMPING SYSTEM
TO INERT GAS COOLING
ELECTRICAL LEADS
CARBON RESISTORS
REMOVABLE END CLOSURE
TRACK
HEARTH CAR
FURNACE CHARGE

Figure 19. Vacuum furnace for the production of low-carbon ferrochrome.104

All types of EAFs (open, sealed, semisealed) produce emissions consisting of a variety of compounds, including POM, in both gaseous and particulate forms. Baghouses were used to control emissions from 87 percent of the open-arc ferroalloy furnaces operating in 1980. Testing of these control systems indicates total particulate removal efficiency of over 99 percent. Such systems should be very effective at controlling POM compounds adsorbed onto fine particulate matter emissions. High pressure-drop venturi scrubbers and electrostatic precipitators have also been applied to open-arc furnaces producing ferroalloys. Reported total particulate matter collection efficiencies for scrubbers ranged from 94 to 98 percent. When ESPs were used, the gas was conditioned with ammonia to enhance particulate resistivity and increase collection efficiency. Estimated total particulate matter removal efficiencies for the ESPs were 98 percent.[99,103-105]

In the case of semisealed furnaces (Figure 16), offgases are drawn from beneath the furnace cover through ducts leading to a control device. However, fugitive particulates and fumes escape through the openings around the electrodes. In some instances, hoods have been placed above the furnaces to capture these emissions. Wet scrubbers, including both multistage centrifugal scrubbers and venturi scrubbers, have been used on semisealed ferroalloy furnaces. Up to 99 percent total particulate matter removal efficiency has been reported for centrifugal scrubbers. Venturi units can exhibit even greater efficiencies.

Venturi scrubbers are commonly used to control emissions from sealed ferroalloy EAFs; however, the use of baghouses at a few installations has occurred. In general, total uncontrolled emissions vented to a control device from a sealed furnace are less than from other ferroalloy EAFs because no air enters sealed furnaces. Resultant gas flows (volumes) to the control device are only 2 to 5 percent of those from open furnaces.[103]

Emission Factors

Polycyclic organic matter emission factor data were identified for a sealed and a semisealed ferroalloy manufacturing EAF. The sealed unit was tested during the production of silicomanganese and during the production of ferromanganese. A high pressure drop wet scrubber was used to control sealed furnace emissions regardless of the ferroalloy being produced. Controlled POM emissions during silicomanganese production were measured to be 1.0 g/Mw-h of energy consumed by the furnace. Pre-scrubber POM emissions from ferromanganese production were 156 g/Mw-h. In the controlled POM emissions sample, fluorene and anthracene were dominant, constituting, respectively, 36 and 51 percent of total POM emissions. Seventy percent of the uncontrolled emissions sample consisted of anthracene (35 percent) and fluoranthene (35 percent).[99,103]

The semisealed ferroalloy furnace tested produced 50 percent ferrosilicon and was controlled by a low energy wet scrubber followed by a flare. Measurements taken after the scrubber but prior to the flare showed total POM emissions to be 91.0 g/Mw-h. Fluorene constituted 50 percent of the total POM quantity, followed by pyrene at 19 percent, fluoranthene at 18 percent, and anthracene and phenanthrene at 12 percent.[99,103]

A POM species specific list of the compounds and quantities measured during testing of ferroalloy EAFs is presented in Table 46.[99,103]

Source Locations

The latest information published by the U. S. Bureau of Mines (BOM) on the locations of ferroalloy manufacturing facilities in the United States is given in Table 47.[106] According to these data, as of 1984 there were 46 ferroalloy facilities in the United States operated by a total of 30 companies. Ohio and Pennsylvania contain the most ferroalloy facilities with seven in each State. Ohio, Pennsylvania, Tennessee, and Alabama together contain almost 57 percent of the total number of facilities nationwide.[106]

TABLE 46. POM EMISSION FACTORS FOR ELECTRIC ARC FURNACES PRODUCING FERROALLOYS[99,103]

POM Compounds	POM Emission Factor - Semisealed Furnace[a,b]		POM Emission Factor - Sealed Furnace[b]			
			Furnace 1[c]		Furnace 2[d]	
	mg/Nm^3	g/Mw-h[e]	mg/Nm^3	g/Mw-h[e]	mg/Nm^3	g/Mw-h[e]
Fluorene	75.0	45.9	1.5	0.36	16.0	4.0
Carbazole	---[f]	---	---	---	9.6	2.4
Anthracene	18.3	11.2	2.1	0.51	220.0	54.9
Phenanthrene	18.3	11.2	---	---	---	---
Cyclopenta(d,e,f)phenanthrene	10.7	6.5	---	---	---	---
Methylanthracenes	1.5	0.92	0.070	0.017	24.0	6.0
Fluoranthene	27.4	16.7	0.24	0.058	220.0	54.9
Pyrene	28.5	17.4	0.22	0.053	2.3	0.57
Methylpyrene	0.07	0.04	0.005	0.0012	14.0	3.5
Benzo(g,h,i)fluoranthene	8.9	5.4	---	---	---	---
Benzo(a) and benzo(b)fluorene	1.24	0.75	---	---	---	---
Chrysene	8.1	4.9	0.016	0.0039	49.0	12.0
Benz(a)anthracene	10.5	6.4	---	---	---	---
Methylchrysenes	---	---	---	---	5.2	1.3
7,12-Dimethylbenz(a)anthracene	---	---	---	---	0.58	0.14
Benzo(e)pyrene	0.81	0.49	---	---	51.0	13.0
Benzofluoranthene	---	---	---	---	---	---
Benzo(f)fluoranthene	3.5	2.1	---	---	---	---
Benzo(k)fluoranthene	0.16	0.10	---	---	---	---
Benzo(e)acephenanthylene	3.5	2.1	---	---	---	---
Perylene	0.43	0.26	---	---	3.1	0.77

TABLE 46. POM EMISSION FACTORS FOR ELECTRIC ARC FURNACES PRODUCING FERROALLOYS[99,103] (Continued)

POM Compounds	POM Emission Factor - Semisealed Furnace[a,b]		POM Emission Factor - Sealed Furnace[b]			
			Furnace 1[c]		Furnace 2[d]	
	mg/Nm^3	g/Mw-h[e]	mg/Nm^3	g/Mw-h[e]	mg/Nm^3	g/Mw-h[e]
Benzo(a)pyrene	1.64	1.0	---	---	---	---
Methylbenzopyrenes	---	---	---	---	1.2	0.30
3-Methylcholanthrene	---	---	---	---	0.39	0.10
Indeno(1,2,3-c,d)pyrene	1.10	0.67	---	---	6.0	1.5
Benzo(g,h,i)perylene	3.2	1.9	---	---	1.4	0.35
Anthanthrene	0.83	0.51	---	---	---	---
Dibenzo(a,h)anthracene	---	---	---	---	0.90	0.22
Dibenzo(c,g)carbazole	---	---	---	---	0.079	0.020
Dibenzo(ai+ah)pyrenes	---	---	---	---	0.54	0.13
Coronene	1.0	0.61	---	---	0.51	0.13
TOTAL POM		91.0		1.0		156.0

[a] Furnace is producing a 50 percent ferrosilicon ferroalloy. POM measurements represent emissions from a low energy wet scrubber used to control the furnace.

[b] POM emission factors represent particulate and gaseous POM species measured during source tests.

[c] Furnace is producing a silicomanganese ferroalloy. POM measurements represent emissions from a high pressure drop wet scrubber used to control the furnace.

[d] Furnace is producing a ferromanganese ferroalloy. POM measurements represent uncontrolled emissions from the furnace.

[e] Emission factors are expressed as grams (g) of POM per megawatt-hour (Mw-h) of energy consumed by the furnace.

[f] Dashes indicate that the compound was not detected.

TABLE 47. LOCATIONS OF FERROALLOY PRODUCERS IN THE UNITED STATES IN 1984

Producer	Plant Location	Type of Furnace
FERROALLOYS		
Affiliated Metals and Minerals, Inc.	New Castle, PA	Metallothermic
Aluminum Company of America, Northwest Alloys, Inc.	Addy, WA	Electric
AMAX, Inc., Climax Molybdenum Company Division	Langeloth, PA	Metallothermic
Ashland Chemical Company	Columbus, OH	Electric and metallothermic
Cabot Corporation, KBI Division, Penn Rare Metal Division	Revere, PA	Metallothermic
Dow Corning Corporation	Springfield, OR	Electric
Elkem A/S, Elkem Metals Company	Alloy, WV Ashtabula, OH Marietta, OH Niagara Falls, NY	Electric and electrolytic
Foote Mineral Company, Ferroalloys Division	Cambridge, OH Graham, WV Keokuk, IA New Johnsonville, TN	Electric and electrolytic
Hanna Mining Company		
Hanna Nickel Smelting Company	Riddle, OR	Electric
Silicon Division	Wenatchee, WA	Electric
International Minerals and Chemical Corporation, Industry Group, TAC Alloys Division	Bridgeport, AL Kimball, TN	Electric Electric
A. Johnson and Company, Inc.	Lionville, PA	Electric
Kerr-McGee Chemical Corporation	Hamilton (Aberdeen), MS	Electrolytic
Macalloy, Inc.	Charleston, SC	Electric

TABLE 47. LOCATIONS OF FERROALLOY PRODUCERS IN THE UNITED STATES IN 1984 (Continued)

Producer	Plant Location	Type of Furnace
Metallurg, Inc., Shieldalloy Corporation	Newfield, NJ	Metallothermic
Moore McCormack Resources, Inc., Globe Metallurgical, Inc.	Beverly, OH Selma, AL	Electric Electric
Ohio Ferro-Alloys Corporation	Montgomery, AL Philo, OH Powhatan Point, OH	Electric
Pennzoil Company, Duval Corporation	Sahuarita, AZ	Metallothermic
Reactive Metals and Alloys Corporation	West Pittsburg, PA	Electric
Reading Alloys, Inc.	Robesonia, PA	Metallothermic
Reynolds Metals Company	Sheffield, AL	Electric
SEDEMA S.A., Chemetals Corporation	Kingwood, WV	Fused-salt electrolytic
SKW Alloys, Inc.	Calvert City, KY Niagara Falls, NY	Electric
Teledyne, Inc., Teledyne Wah Chang, Albany Division	Albany, OR	Metallothermic
Union Carbide Corporation, Metals Division	Marietta, OH Niagara Falls, NY	Electric
Union Oil Company of California, Molycorp, Inc.	Washington, PA	Electric and metallothermic
FERROPHOSPHORUS		
Electro-Phos Corporation	Pierce, FL	Electric
FMC Corporation, Industrial Chemical Division	Pocatello, ID	Electric
Monsanto Company, Monsanto Industrial Chemicals Company	Columbia, TN Soda Springs, ID	Electric Electric

TABLE 47. LOCATIONS OF FERROALLOY PRODUCERS IN THE UNITED STATES IN 1984 (Continued)

Producer	Plant Location	Type of Furnace
Occidental Petroleum Corporation, Hooker Chemical Company, Industrial Chemicals Group	Columbia, TN	Electric
Stauffer Chemical Company, Industrial Chemical Division	Mount Pleasant, TN	Electric
	Silver Bow, MT	Electric
	Tarpon Springs, FL	Electric

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

IRON AND STEEL FOUNDRIES

Process Description

Iron and steel foundries can be defined as those which produce gray, white, ductile, or malleable iron and steel castings. Cast iron and steels are both solid solutions of iron, carbon, and various alloying materials. Although there are many types of each, the iron and steel families can be distinguished by their carbon content. Cast irons typically contain 2 percent carbon or greater; cast steels usually contain less than 2 percent carbon.[107]

Iron castings are used in almost all types of equipment, including motor vehicles, farm machinery, construction machinery, petroleum industry equipment, electrical motors, and iron and steel industry equipment. Steel castings are classified on the basis of their composition and heat treatment, which determine their end use. Steel casting classifications include carbon, low alloy, general purpose structural, heat resistant, corrosion resistant, and wear resistant. They are used in motor vehicles, railroad equipment, construction machinery, aircraft, agricultural equipment, ore refining machinery, and chemical manufacturing equipment.[107]

The following four basic operations are performed in all iron and steel foundries.

- storage and handling of raw materials
- melting of the raw materials
- transfer of the hot molten metal into molds
- preparation of the molds to hold the molten metal

Other processes present in most, but not all, foundries include:

- sand preparation and handling;
- mold cooling and shakeout;

- casting cleaning, heat treating, and finishing;
- coremaking; and
- pattern making.

A generic process flow diagram for iron and steel foundries is given in Figure 20.[107]

Iron and steel castings are produced in a foundry by injecting or pouring molten metal into cavities of a mold made of sand, metal, or ceramic material. Input metal is melted by the use of a cupola, an electric arc furnace, or an induction furnace. About 70 percent of all iron castings are produced using cupolas, with lesser amounts produced in electric arc and induction furnaces. However, the use of electric arc furnaces in iron foundries is increasing. Steel foundries rely almost exclusively on electric arc or induction furnaces for melting purposes. With either type of foundry, when the poured metal has solidified, the molds are separated and the castings removed from the mold flasks on a casting shakeout unit. Abrasive (shotblasting) cleaning, grinding, and heat treating are performed as is necessary. The castings are then inspected and shipped to another industry for machining and/or assembly into a final product.[107]

In a typical foundry operation, charges to the melting unit are sorted by size and density and cleaned (as required) prior to being put in the melter. Charges consist of scrap metal, ingot, carbon (coke), and flux. Prepared charge materials are placed in crane buckets, weighed, and transferred into the melting furnace or cupola. The charge in a furnace or cupola is heated until it reaches a certain temperature and the desired chemistry of the melt has been attained. Once the desired product is obtained, the molten metal is either poured out of the furnace into various sized teeming ladles and then into the molds or it is transferred to holding furnaces for later use.

The casting or mold pouring operation in iron and steel foundries has been determined to be a source of POM emissions.[108-111] The origin of these POM emissions is suspected to be the organic binders, including coal powder

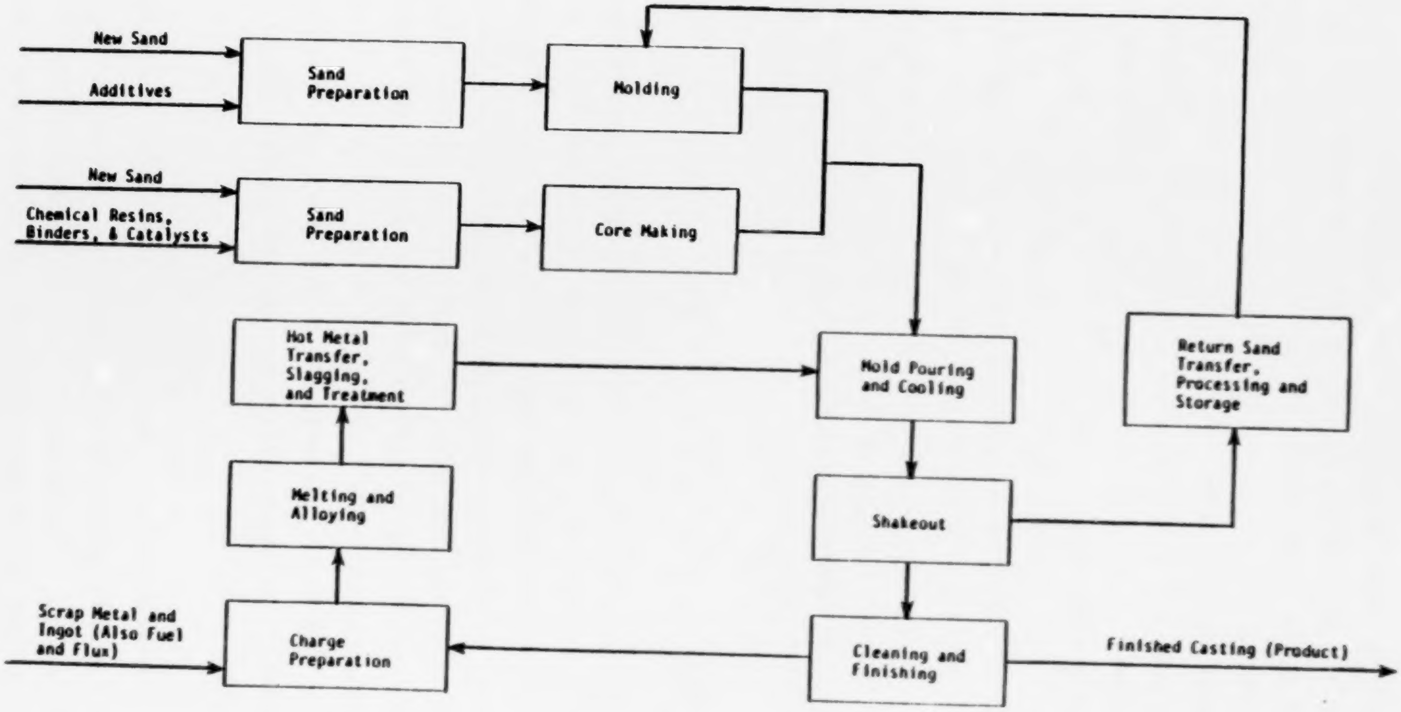

New Sand
Additives
Sand Preparation
Molding
New Sand
Chemical Resins, Binders, & Catalysts
Sand Preparation
Core Making
Hot Metal Transfer, Slagging, and Treatment
Mold Pouring and Cooling
Return Sand Transfer, Processing and Storage
Melting and Alloying
Shakeout
Scrap Metal and Ingot (Also Fuel and Flux)
Charge Preparation
Cleaning and Finishing
Finished Casting (Product)

Figure 20. Typical process flow diagram for a sand-cast iron and steel foundry.[107]

and coal tar pitch, used to form the sand molds used for molten metal casting. When the hot molten metal contacts the sand mold pyrolysis occurs and a plume of smoke is generated which contains a rich mixture of organic compounds including POMs. In addition to casting, mold preparation and casting shakeout (removal from the mold) activities have also been determined to generate POM emissions. Potential POM emissions from molding and casting appear to be a function of the type and quantity of organic binder used to produce casting molds.[108-111]

Emissions of POM from mold preparation, casting, and shakeout operations are fugitive in nature and likely exist in both particulate and gaseous forms. Fugitive emissions from such sources are generally controlled with local hooding or building ventilation systems that are ducted to a control device (predominantly baghouses) or to the atmosphere.[107-111]

Emission Factors

No POM emission factor data for iron and steel foundries could be found in the literature. However, the existence of POM emissions from molding and casting operations has been confirmed by air sampling of worker breathing zones and plant areas associated with these operations. The air sampling that has been conducted has measured only particulate POM compounds. As many as 50 POM species have been detected in foundry air samples.[109] Predominant POM compounds that have been detected include benzo(a)pyrene, benzo(e)pyrene, perylene, phenanthrene, anthracene, fluoranthrene, benzofluoranthenes, dibenzanthracenes, benzochrysenes, benzo(g,h,i)perylene, and o-phenylenepyrene.[109]

In the quantitative data that are available, POM emissions from using a coal tar pitch binder appear to be greater than those associated with using a coal powder binder.[109] The concentration of benzo(a)pyrene in the workplace air of two foundries using coal tar pitch binders ranged from less than 0.01 to 72 ug/m^3 of air. The average level was 5 ug/m^3.[109] The level of benzo(a)pyrene as a function of the mass of particulate matter sampled ranged from less than 0.01 to 6.7 ug/mg, with the average being 1.1 ug/mg.[109]

In four foundries using a coal powder binder, workplace air had a benzo(a)pyrene level of less than 0.01 to 0.82 ug/m^3 of air.[108] The average level was 0.08 ug/m^3. The concentration of benzo(a)pyrene in sampled particulate matter ranged from less than 0.01 to 0.32 ug/mg, with the average being 0.03 ug/mg.[108]

Source Locations

The 1980 U. S. EPA background information document for new source performance standards covering electric arc furnaces in ferrous foundries indicated that there were approximately 4400 iron and steel foundries in the United States.[107] The States with the greatest percentage of foundries are:

- Ohio (10.3 percent)
- California (9.7 percent)
- Pennsylvania (8.4 percent)
- Michigan (7.9 percent)
- Illinois (7.2 percent)
- New York (6.0 percent)
- Wisconsin (4.4 percent)
- Indiana (4.4 percent)

As evidenced by these States, foundry locations can be correlated with areas of heavy industry and manufacturing, and in general, with the iron and steel production industry (Ohio, Pennsylvania, and Indiana).

Additional information on iron and steel foundries and their locations may be obtainable from the following trade associations.

- American Foundrymen's Society, Des Plaines, Illinois
- National Foundry Association, Des Plaines, Illinois

- Ductile Iron Society, Mountainside, New Jersey
- Iron Casting Society, Warrendale, Pennsylvania
- Steel Founders' Society of America, Des Plaines, Illinois

BY-PRODUCT COKE PRODUCTION

Process Description

The by-product coke production source category includes processes used to treat coal to produce coke and the recovery and treatment of by-product gases from coking to generate secondary products such as crude tars, light oil, and ammonia. Coke is one of the basic raw materials used in blast furnaces to convert iron ore into iron. Approximately 92 percent of the coke produced in the United States is used for this purpose. Other than blast furnaces, coke is principally used in iron foundries, nonferrous smelters, and the chemical industry.[112]

In the United States, coke is produced by two methods: the contemporary by-product recovery or slot oven process and the original beehive process. Currently, the slot oven process accounts for approximately 99 percent of the annual metallurgical coke production in the United States.

The coking industry is generally classified into two sectors, furnace and merchant. Furnace plants are owned by or affiliated with iron- and steel-producing companies that produce coke primarily for consumption in their own blast furnaces, although they also engage in some intercompany sales among steel firms with excesses or deficits in coke capacity.[112] In 1984, there were 28 furnace plants, which accounted for roughly 92 percent of the total coke production. Independent merchant plants produce coke for sale on the open market and are typically owned by chemical or coal firms. The 15 merchant plants in existence in 1984 accounted for about 8 percent of the total coke produced. These firms sell most of their products to other firms engaged in blast furnace, foundry, and nonferrous smelting operations.[112]

By-product recovery coking facilities contain three major processing operations: coal preparation and charging, thermal distillation of coal (coking), and recovery of coking by-products. A generalized process flow diagram for by-product recovery operations is shown in detail in Figure 21.[112] Although not shown in detail in Figure 21, coal preparation and charging is the initial operation in by-product recovery coking plants. The coal that is charged to the by-product coke ovens is usually a blend of two or more low, medium, or high volatile coals that are generally low in sulfur and ash. Blending is required to control the properties of the resulting coke, to optimize the quality and quantity of by-products, and to avoid the expansion exhibited by types of coal that may cause excessive pressure on the oven walls during the coking process.

Coal is usually received on railroad cars or barges. Conveyor belts transfer the coal as needed from the barges or from a coal storage pile to mixing bins where the various types of coal are stored. The coal is transferred from the mixing bins to a crusher where it is pulverized to a preselected size between 0.15 and 3.2 mm (0.006 to 0.13 in). The desired size depends on the response of the coal to coking reactions and the ultimate coke strength that is required.[112]

The pulverized coal is then mixed and blended, and sometimes water and oil are added to control the bulk density of the mixture. The prepared coal mixture is transported to coal storage bunkers on the coke oven batteries. A weighed amount or volume of prepared coal is discharged from the bunker into a larry car, a vehicle which is driven by electric motors and travels the length of the battery top on a wide gauge railroad track. The larry car is positioned over the empty, hot oven, the lids on the charging ports are removed, and the coal is discharged from the hoppers of the larry car through discharge chutes. The flow rate from the hoppers to the oven may be controlled by gravity, a rotary table, or screw feeders. To prevent gases from escaping during charging, a steam-jet aspirator is used in most plants to draw gases from the space above the charged coal into the collecting main.[112]

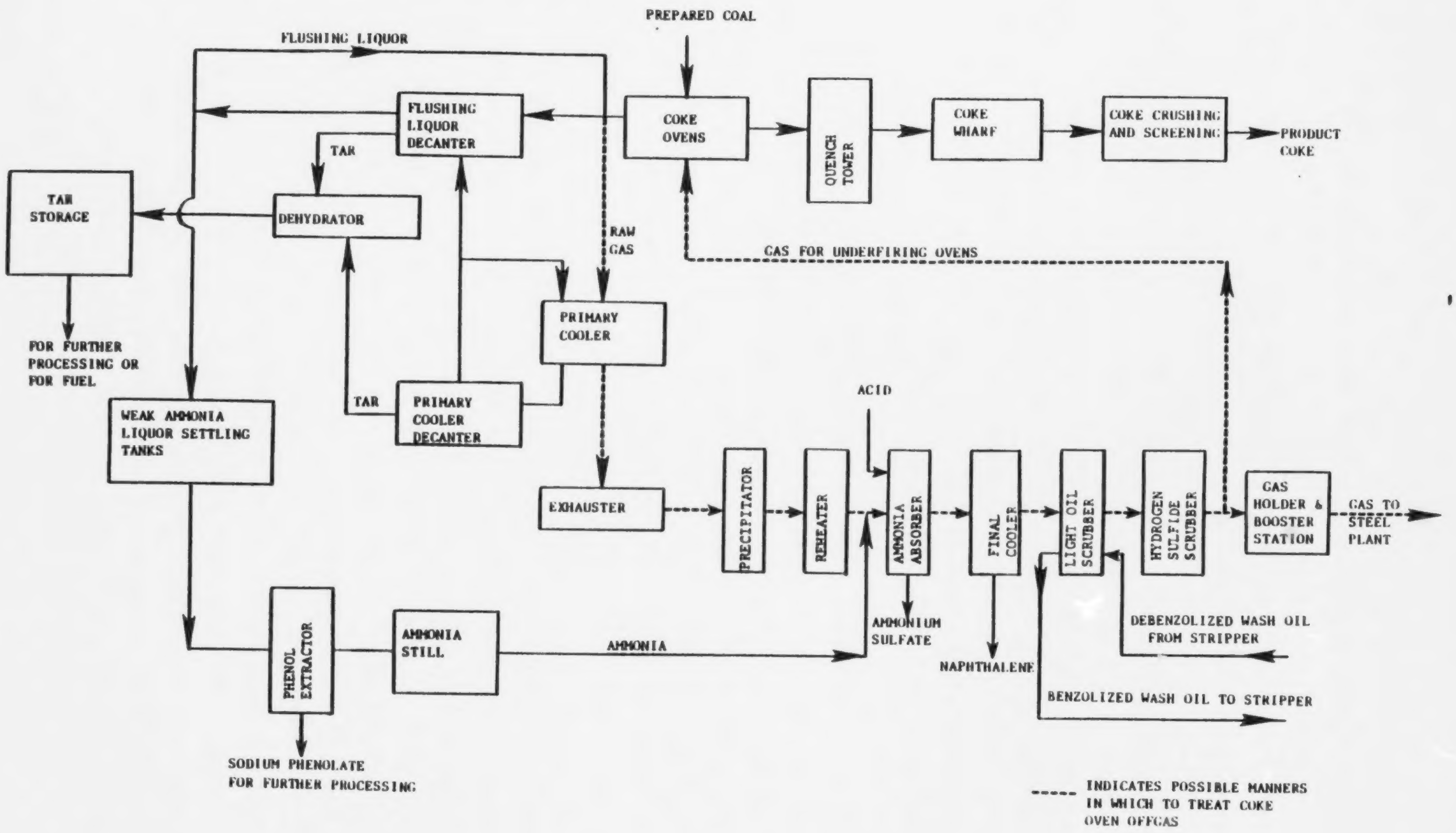

PREPARED COAL
FLUSHING LIQUOR
FLUSHING LIQUOR DECANTER
COKE OVENS
QUENCH TOWER
COKE WHARF
COKE CRUSHING AND SCREENING
PRODUCT COKE
TAR
TAR STORAGE
DEHYDRATOR
RAW GAS
GAS FOR UNDERFIRING OVENS
PRIMARY COOLER
FOR FURTHER PROCESSING OR FOR FUEL
TAR
PRIMARY COOLER DECANTER
ACID
WEAK AMMONIA LIQUOR SETTLING TANKS
EXHAUSTER
PRECIPITATOR
REHEATER
AMMONIA ABSORBER
FINAL COOLER
LIGHT OIL SCRUBBER
HYDROGEN SULFIDE SCRUBBER
GAS HOLDER & BOOSTER STATION
GAS TO STEEL PLANT
PHENOL EXTRACTOR
AMMONIA STILL
AMMONIA
AMMONIUM SULFATE
NAPHTHALENE
DEBENZOLIZED WASH OIL FROM STRIPPER
BENZOLIZED WASH OIL TO STRIPPER
SODIUM PHENOLATE FOR FURTHER PROCESSING
INDICATES POSSIBLE MANNERS IN WHICH TO TREAT COKE OVEN OFFGAS

Figure 21. General process flow diagram for a by-product coke plant.[112]

Peaks of coal will form directly under the charging ports as the oven is filled. These peaks are leveled by a steel bar that is cantilevered from the pusher machine through an opening called the chuck door on the pusher side of the battery. This leveling process provides a clear vapor space and exit tunnel for the gases that evolve during coking to flow to the standpipes and aids in the uniform coking of the coal. After filling, the chuck door and the topside charging ports are closed. In some plants, the charging ports are sealed with a wet clay mixture called luting.[112]

The thermal distillation or coking of coal to separate volatile and nonvolatile components takes place in coke ovens that are grouped in batteries. A battery consists of 20 to 100 adjacent ovens with common side walls which contain integral flues. Coke oven heating systems fall into two general classes: underjet and gun-flue. In the underjet heating system, the flue gas is introduced into each flue from piping in the basement of the battery. The gas flow to each flue can be metered and controlled. The gun-flue heating system introduces the gas through a horizontal gas duct extending the length of each wall slightly below the floorline of each oven. Short ducts lead upward to a nozzle brick at the bottom of each of the vertical flues in an oven.[112]

Heat for the coking operation is provided by a regenerative combustion system located below the ovens. Because the combustion flue gas contains a significant amount of process heat, two heat regenerators are used for recovery. These regenerators are located below each oven, one for combustion air and one for the combustion waste gas. The flow is alternated between the two at about 30 minute intervals. The slot ovens operate like chemical retorts in that they are both batch operated, fitted with exhaust flues (standpipes), and function without the addition of any reagent.

The operation of each oven in the battery is cyclic, but the batteries usually contain a sufficiently large number of ovens (an average of 57) so that the yield of by-products is essentially continuous. The individual ovens are charged and discharged at approximately equal time intervals during the coking cycle. The resultant constant flow of evolved gases from all the ovens in a battery helps to maintain a balance of pressure in the flues, collecting main, and stack. All of the ovens are fired continuously at a constant rate, irrespective of a particular oven's stage in the coking cycle. If damage to the refractory occurs in inaccessible locations through overheating or expansion of coal, repairs may be extremely difficult. A cooldown takes from 5 to 7 weeks, so a battery shutdown is undertaken only as a last alternative.[112]

After the ovens are filled, coking proceeds for 15 to 18 hours to produce blast furnace coke and 25 to 30 hours to produce foundry coke. The coking time is determined by the coal mixture, moisture content of the coal, rate of underfiring, and the desired properties of the coke. The coking temperatures generally range from 900 to 1100°C (1652 to 2012°F) and are kept on the high side of the range to produce blast furnace coke. Air is prevented from leaking into the ovens by maintaining a positive back pressure of about 10 mm (0.4 in) water. The gases and hydrocarbons that are evolved during thermal distillation are removed through the offtake main and sent to the by-product plant for recovery.[112]

At the end of the coking cycle, doors at both ends of the oven are removed and the incandescent coke is pushed out the coke side of the oven by a ram which is extended from the pusher machine. The coke is pushed through a coke guide into a special railroad car, called a quench car, which traverses the coke side of the battery. The quench car carries the coke to the end of the battery to a quench tower where it is deluged with water so that it will not continue to burn after being exposed to air. The quenched coke is discharged onto an inclined coke wharf to allow excess water to drain and cool the coke to a reasonable handling temperature.[112]

Gates along the lower edge of the wharf control the rate of coke falling on a conveyor belt which carries it to the crushing and screening system. The coke is then crushed and screened to obtain the optimum size for the particular blast furnace operation in which it is to be used. The undersize coke generated by the crushing and screening operations is used in other steel plant processes, stockpiled, or sold.[112]

Gases evolved during coking leave the coke oven through the standpipes, pass into goosenecks, and travel through a damper valve to the gas collection main which directs them to the by-product plant. These gases account for 20 to 35 percent by weight of the initial coal charge and are composed of water vapor, tar, light oils, heavy hydrocarbons, and other chemical compounds.[112,113]

The raw coke oven gas exits at estimated temperatures of 760 to 870°C (1400 to 1598°F) and is shock cooled by spraying recycled flushing liquor in the gooseneck. This spray cools the gas to 80 to 100°C (176 to 212°F), precipitates tar, condenses various vapors, and serves as the carrying medium for the condensed compounds. These products are separated from the liquor in a decanter and are subsequently processed to yield tar and tar derivatives.[112,113]

The gas is then passed either to a final tar extractor or an electrostatic precipitator for additional tar removal. When the gas leaves the tar extractor, it carries 75 percent of the ammonia and 95 percent of the light oil originally present when leaving the oven.

The ammonia is recovered either as an aqueous solution by water absorption or as ammonium sulfate salt. Ammonium sulfate is crystallized in a saturator which contains a solution of 5 to 10 percent sulfuric acid and is removed by an air injector or centrifugal pump. The salt is dried in a centrifuge and packaged.

The gas leaving the saturator at about 60°C (140°F) is taken to final coolers or condensers, where it is typically cooled with water to approximately 24°C (75°F). During this cooling, some naphthalene separates and is carried along with the wastewater and recovered. The remaining gas is passed into a light oil or benzol scrubber, over which is circulated a heavy petroleum fraction called wash oil or a coal-tar oil which serves as the absorbent medium. The oil is sprayed in the top of the packed absorption tower while the gas flows up through the tower. The wash oil absorbs about 2 to 3 percent of its weight of light oil, with a removal efficiency of about 95 percent of the light oil vapor in the gas. The rich wash oil is passed to a countercurrent steam stripping column. The steam and light oil vapors pass upward from the still through a heat exchanger to a condenser and water separator. The light oil may be sold as crude or processed to recover benzene, toluene, xylene, and solvent naphtha.[112,113]

After tar, ammonia, and light oil removal, the gas undergoes a final desulfurization process at some coke plants before being used as fuel. The coke oven gas has a rather high heating value, on the order of 20 MJ/Nm^3 (550 $Btu/stdft^3$). Typically, 35 to 40 percent of the gas is returned to fuel the coke oven combustion system, and the remainder is used for other plant heating needs.[112,113]

During by-product recovery plant coking, POM emissions are most likely to occur from coal charging operations, oven door leaks, topside leaks, coke pushing operations, coke quenching operations, and battery stacks. The control of emissions from these sources is generally achieved by using one or a combination of the following control alternatives.[112,114]

- containment of emissions in the process
- capture techniques (e.g., hoods and enclosures)
- add-on control devices
- process changes

The applicability of these alternatives to each of the POM-emitting coking operations is described in Table 48.[114] The effectiveness of the control measures in Table 48 is likely to vary from plant to plant due to differences in plant configurations and in the types of POM present in emissions. Data provided in Reference 115 clearly shows that not all POM

TABLE 48. EMISSION CONTROLS USED ON POM EMISSION SOURCES IN BY-PRODUCT COKE PLANTS[114]

POM Emission Source	Type of Control Needed	Emission Control Techniques
Coal Charging	Containment	Use of staged charging and aspiration to draw emissions into the coke battery.
Door Leaks	Containment/Capture and Control Devices	Use and maintenance of doors designed to close and seal tightly. Use of collection hoods on individual doors. Use of wet scrubber and wet ESP control devices on collected emissions.[a]
Topside Leaks	Containment	Application and maintenance of sealing compounds to leaking points.
Coke Pushing	Containment/Capture and Control Devices	Use of enclosures over the coke side of the battery. Use of wet scrubber and wet ESP control devices on collected emissions.
Coke Quenching	Process Changes	Use of single or multiple baffles in the quench tower and use of only clean water for quenching. Dry quenching is another option; however, it would require additional capture and control devices.
Battery Stacks	Containment and/or Control Devices	Patching cracks in oven walls as needed and treat exhaust gases in wet scrubbers, ESPs, or baghouses.

---

[a] In a coking facility using a wet ESP to control oven door emissions, the ESP was found to reduce total POM emissions an average of 69 percent (range of 17.2-92.4 percent). If the naphthalene component of total POM is excluded, the total POM control efficiency average is 95.6 percent (range of 93.5-98.8 percent).

compounds in an emissions stream are controlled to the same extent (see footnote a in Table 48). Examples of the type of POM compounds measured in coking emissions are given in Tables 49, 50, and 51.[114-117]

In the by-products recovery section of a coking plant, the tar processing operation, the ammonia processing operation, and the final cooler/naphthalene handling operation have been identified as potential sources of POM emissions.[113] In tar processing, tar decanting, tar dewatering and storage, and tar distillation operations are potential POM emission sources. Emissions are fugitive in nature and are generally released directly to the atmosphere.[113]

Excess ammonia liquor treatment has been determined to be a source of POM emissions during ammonia processing. Specifically, steam stripping of the liquor to recover ammonia has been found to generate POM emissions. In the final cooling/naphthalene handling operations, the cooling tower for the contact cooler and froth flotation naphthalene separator are potential POM emission sources. Coke oven gas is cooled by means of a direct contact spray tower cooler. After contacting the coke oven gas in the final cooler, the water is pumped to a separation device prior to being sent to a cooling tower. Froth flotation is used to enhance naphthalene separation. Fugitive POM emissions are potentially released from the froth flotation process.[113]

After separation of the naphthalene, the contact water is sent to an atmospheric cooling tower prior to being returned to the spray tower cooler. The cooling tower operation is a potential source of POM emissions because organic components dissolved in the recirculating water will be air stripped and released into the atmosphere.[113]

Emission Factors

Limited emission factor data exist for total POM or individual POM species emissions from coking and by-product recovery processes. Available POM data for slot oven coking sources and for by-product recovery sources

TABLE 49. SPECIFIC POM COMPOUNDS DETECTED IN OVEN DOOR LEAK EMISSIONS[114-117]

POMs in Controlled Door Leak Emissions	POMs in Uncontrolled Door Leak Emissions
Naphthalene	Benzo(a)phenanthrene
Fluoranthene	Benzo(e)pyrene
Pyrene	Benzofluoranthenes
Benz(c)phenanthrene	Benzo(k)fluoranthene
Chrysene	Chrysene
Benz(a)anthracene	Dibenzanthracenes
7,12-Dimethylbenz(a)anthracene	Dibenzpyrene
Benzofluoranthenes	Dimethylbenz(a)anthracene
Benzo(a)pyrene	Fluoranthene
Benzo(e)pyrene	Indeno(1,2,3-c,d)pyrene
Cholanthrene	Naphthalene
Indeno(1,2,3-c,d)pyrene	Pyrene
Dibenz(a,h)anthracene	Benzo(a)pyrene
Dibenzacridines	
Dibenz(c,g)carbazole	
Dibenzpyrenes	
3-Methyl cholanthrene	

TABLE 50. POM COMPOUNDS DETECTED IN BATTERY TOPSIDE EMISSIONS[114-117]

Phenanthrene
Anthracene
Methylphenanthrene/methylanthracene
Fluoranthene
Dihydrobenzo(a,b)fluorene
Pyrene
Benzo(a)fluorene
Benzo(b)fluorene
Benzo(c)phenanthrene
Benz(a)anthracene
Chrysene/triphenylene
Benzo(b,j,k)fluoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
o-Phenylenepyrene
Benzo(g,h,i)perylene
Anthanthrene
Coronene
Dibenzopyrene

TABLE 51. SPECIFIC POM COMPOUNDS DETECTED IN QUENCH TOWER EMISSIONS[114-117]

Anthracene
Methyl anthracenes
Fluoranthene
Pyrene
Methyl pyrene and fluoranthene
Benzo(c)phenanthrene
Chrysene and benz(a)anthracene
Methyl chrysenes
Dimethylbenz(a)anthracene
Benzo(a)pyrene
3-Methyl cholanthrene
7,12-Dimethylbenz(a)anthracene
Dibenz(a,h)anthracene
Dibenzo(a,h)pyrene
Dibenzo(a,i)pyrene
Benz(a)anthracenes
Pyridine
Indeno(1,2,3-c,d)pyrene
Phenanthrene
Phenol
Cresol
Quinoline

are given in Tables 52 and 53, respectively.[112,114-116,118-120] The lack of substantive POM emissions data for coking sources prohibits extensive characterization and comparison; however, as indicated in Table 52, POM emissions from coking processes are highly variable because coking conditions can vary widely from plant to plant and within the same plant from process to process. Coal composition and moisture content vary widely and these process variables can have a significant bearing on emissions. Coking times and temperatures can also be varied so as to have marked impacts on potential POM emissions. The fugitive nature of the majority of coking process POM emissions complicates emissions control and increases the potential for widely varying emission estimates. For coke oven sources, specific source emissions testing should be utilized if possible to characterize POM emissions.

Although data for POM emissions from coke by-product recovery processes are also few, it is anticipated that emissions would be as equally variable as in coking sources. Emissions of POM from the by-product plant are in large part a function of the raw coke gas entering the recovery process. As the composition of this stream changes with the coking process, so would potential POM emissions from by-product recovery.

Source Locations

As of the end of 1984, 43 by-product coke plants with 143 coking batteries were in existence in the United States. Of these 43, 36 were in operation.[112] Table 54 lists the existing installations, their classification as merchant or furnace plants, and the major uses of their coke. In terms of production, almost 60 percent of the coke produced in the United States occurs in Indiana, Pennsylvania, and Ohio. In 1983, Indiana was the leading coke producing State with 23 percent of the national total.[112]

TABLE 52. POM EMISSION FACTOR DATA FOR SLOT OVEN COKING SOURCES

Emission Source	Total POM Emission Factor	Benzo(a)pyrene Emission Factor	Comments	Reference
Door Leaks	5,524 ng/Nm^3 [a,b]	141 ng/Nm^3 [a]	Uncontrolled[c]	115
Door Leaks	1,256 ng/Nm^3 [a,d]	1.8 ng/Nm^3 [a]	Controlled by a wet ESP[e]	115
Door Leaks	4.3 g/Mg of coal charged[f]	0.0018 to 1.4 g/Mg of coal charged	Control status unknown	118
Door Leaks	0.00007 g/Mg of coal charged[g]	Not available	Controlled by a wet ESP	112
Coke Quenching	0.002 to 0.009 g/Mg of coal charged[h]	0.0005 g/Mg of coal charged	---	118
Coke Quenching	1.85 g/Mg of coal charged[i]	Not available	Clean water used for quench	114
Coke Quenching	613 g/Mg of coal charged[i]	Not available	Contaminated water used for quench	114
Battery Stacks	Not available	0.002 to 0.02 g/Mg of coal charged	---	118
Door Leaks	Not available	0.054 g/Mg of coke produced[j]	German coke oven equipped with conventional rigid seal doors	119
Door Leaks	Not available	0.01 g/Mg of coke produced[j]	German coke oven equipped with spring loaded door seals	119
Door Leaks	0.11 g/Mg of coke produced[j]	0.015 g/Mg of coke produced[j]	German coke oven equipped with spring loaded door seals	119
Coke Oven Emissions	25,260 ug/g of sample collected[j,k]	1,765 ug/g of sample collected[j]	Specific sources were not identified	116, 120

[a] Average of four test runs.

[b] Principal POM species measured were naphthalene, fluoranthrene, pyrene, and benzofluoranthenes.

[c] Of total uncontrolled POM emissions, 77 percent were in particulate form and 23 percent were in gaseous form.

[d] Principal POM species measured were naphthalene, fluoranthrene, and pyrene.

[e] Of total controlled POM emissions, 98 percent were in gaseous form and 2 percent were in particulate form.

[f] Constituents of total POM include benzo(a)phenanthrene, benzo(e)pyrene, benzofluoranthenes, benzo(k)fluoranthene, chrysene, dibenzanthracenes, dibenzpyrene, dimethylbenz(a)anthracene, fluoranthene, pyrene, naphthalene, benzo(a)pyrene, and indeno(1,2,3-c,d)pyrene.

[g] Constituents of total POM include naphthalene, fluoranthene, pyrene, chrysene, benz(c)phenanthrene, benz(a)anthracene, 7,12-dimethylbenz(a)anthracene, benzofluoranthenes, benzo(a)pyrene, benzo(e)pyrene, cholanthrene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene, dibenzacridines, dibenz(c,g)carbazole, dibenzpyrenes, and 3-methyl cholanthrene.

[h] Constituents of total POM include anthracene, phenanthrene, methyl anthracenes, fluoranthene, pyrene, methyl pyrene/fluoranthene, benzo(c)phenanthrene, methyl chrysenes, benzo(a)pyrene, dimethylbenz(a)anthracene, and chrysene/benz(a)anthracene.

[i] Average of tests for green and non-green coke. Samples were gathered using a modified Method 5 procedure; such results are for particulate and gaseous POM. Constituents of total POM include benzo(a)pyrene, 3-methyl cholanthrene, 7,12-dimethylbenz(a)anthracene, dibenz(a,h)anthracene, dibenzo(a,h)pyrene, dibenzo(a,i)pyrene, benz(a)anthracenes, pyridine, indeno(1,2,3-c,d)pyrene, phenanthrene, phenol, cresol, and quinoline.

[j] Represents particulate POM emissions only.

[k] Seventy-five POM compounds were analyzed for in each of four separate test runs. This value represents the average of the four runs. The predominant POM species consistently detected during the sampling include phenanthrene, fluoranthene, pyrene, benz(a)anthracene, benzo(k)fluoranthene, benzo(b)fluoranthene, and benzo(a)pyrene.

TABLE 53. POM EMISSION FACTOR DATA FOR COKE BY-PRODUCT RECOVERY PROCESSES[113]

POM Emission Source	Total POM Emission Factor, g/Mg[a,b]	Biphenyl Emission Factor, g/Mg[a,b]	Quinoline Emission Factor, g/Mg[a,b]
Tar Processing			
Tar Decanter	4.1[c]	0.03	0.06
Tar Dewatering and Storage	0.003	0.002	0.0006
Tar Distillation Product Storage	0.011	Not available	Not available
Final Cooler/Naphthalene Handling			
Cooling Tower for Contact Cooler	6.4	0.06	0.32

[a] Factors are expressed in terms of g/Mg of coal fed to the coking ovens. Values represent uncontrolled emissions.

[b] Emission factors represent particulate and gaseous POM.

[c] Naphthalene is the major constituent of total POM.

TABLE 54. LOCATIONS OF BY-PRODUCT RECOVERY PROCESS COKE PRODUCTION PLANTS IN THE UNITED STATES IN 1984[112]

Company Name	Plant Location	Classification of Plant	Major Uses of Coke[a]
Armco, Inc.	Ashland, KY	Furnace	Blast furnace
	Middletown, OH (2)[b]	Furnace	Blast furnace
Bethlehem Steel Corporation	Bethlehem, PA	Furnace	Blast furnace
	Burns Harbor, IN	Furnace	Blast furnace
	Lackawanna, NY	Merchant	Blast furnace
	Sparrows Point, MD	Furnace	Blast furnace
Rouge Steel	Dearborn, MI	Furnace	Blast furnace
Inland Steel Company	East Chicago, IN (3)	Furnace	Blast furnace
Interlake, Inc.	Chicago, IL	Furnace	Blast furnace
The LTV Steel Corporation	Aliquippa, PA[c]	Furnace	Blast furnace
	Cleveland, OH (2)	Furnace	Blast furnace
	East Chicago, IN	Furnace	Blast furnace
	Gadsden, AL	Furnace	Blast furnace
	Pittsburgh, PA	Furnace	Blast furnace
	South Chicago, IL	Furnace	Blast furnace
	Thomas, AL	Furnace	Blast furnace
	Warren, OH	Furnace	Blast furnace
Lone Star Steel Company[d]	Lone Star, TX	Furnace	Blast furnace
National Steel Corporation	Granite City, IL	Furnace	Blast furnace
	Detroit, MI	Furnace	Blast furnace
Weirton Steel Corporation	Brown's Island, WV	Furnace	Blast furnace

TABLE 54. LOCATIONS OF BY-PRODUCT RECOVERY PROCESS COKE PRODUCTION PLANTS IN THE UNITED STATES IN 1984[112] (Continued)

Company Name	Plant Location	Classification of Plant	Major Uses of Coke[a]
New Boston Coke Corporation	Portsmouth, OH	Furnace	Blast furnace
U. S. Steel Corporation	Clairton, PA (4)	Furnace	Blast furnace
	Fairfield, AL	Furnace	Blast furnace
	Fairless Hills, PA	Furnace	Blast furnace
	Gary, IN	Furnace	Blast furnace
	Lorain, OH	Furnace	Blast furnace
	Provo, UT	Furnace	Blast furnace
Wheeling-Pittsburgh Steel Corporation	East Steubenville, WV	Furnace	Blast furnace
	Monessen, PA	Furnace	Blast furnace
Jim Walter Corporation	Birmingham, AL	Merchant	Blast furnace, foundry
Koppers Company, Inc.	Erie, PA	Merchant	Foundry, other industrial
	Toledo, OH	Merchant	Foundry
	Woodward, AL	Merchant	Blast furnace, foundry
Shenango, Inc.	Neville Island, PA	Merchant	Blast furnace, foundry
Alabama By-Products Corporation	Tarrant, AL	Merchant	Foundry, other industrial
	Keystone, PA	Merchant	Foundry
Carondelet Coke Corporation	St. Louis, MO	Merchant	Foundry, other industrial
Chattanooga Coke and Chemical Company, Inc.	Chattanooga, TN	Merchant	Foundry, other industrial
Citizens Gas and Coke Utility	Indianapolis, IN	Merchant	Foundry

TABLE 54. LOCATIONS OF BY-PRODUCT RECOVERY PROCESS COKE PRODUCTION PLANTS IN THE UNITED STATES IN 1984[112] (Continued)

Company Name	Plant Location	Classification of Plant	Major Uses of Coke[a]
Detroit Coke Corporation	Detroit, MI	Merchant	Foundry
Empire Coke Company	Holt, AL	Merchant	Foundry
Indiana Gas and Chemical Corporation	Terre Haute, IN	Merchant	Foundry, other industrial
Tonawanda Coke Corporation	Buffalo, NY	Merchant	Foundry

[a] An end use is considered a major use if it is at least 20 percent of the plant's total distribution of coke.

[b] Numbers in parentheses indicate the number of plants at that location. If no number is indicated, only one plant exists at that location.

[c] LTV announced is intention in May 1985 to reduce production of steel at the Aliquippa, Pennsylvania plant. The plant may convert to a cold-idle status eventually.

[d] Northwest Industries, Inc., the parent company of Lone Star Steel, announced in April 1985 its merger with Farley Industries.

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

ASPHALT ROOFING MANUFACTURING

Process Description

Certain processing steps used in the production of asphalt roofing materials have been shown to be potential sources of POM emissions. Emissions of POM compounds result primarily from the heating and air blowing of asphalt mixtures, from asphalt saturation processes, and from evaporation losses during asphalt material storage and handling.

The asphaltic material used to make roofing grades of asphalt, known as saturant and coating asphalt, is a product of the fractional distillation of crude oil. This material is obtained toward the end of the distilling process and is commonly known as asphalt flux. Asphalt flux is sometimes blown by the oil refiner or asphalt processor to meet the roofing manufacturer's specifications. Many roofing manufacturers, however, purchase the flux and carry out their own blowing.[121-123]

Handling and storage activities associated with the asphalt flux raw material are potential sources of organic emissions, including POM. Asphalt is normally delivered to the asphalt roofing plant in bulk by pipeline, tanker truck, or railcar. Bulk asphalts are delivered in liquid form at temperatures of 93 to 204°C (200 to 400°F), depending on the type of asphalt and local practice.[121-123] With bulk liquid asphalt, the most common method of unloading is to couple a flexible pipe to the tanker and pump the asphalt directly into the appropriate storage tanks. The tanker cover is partially open during the transfer. Since this is a closed system, the only potential sources of emissions are the tanker and the storage tanks. The magnitude of the emissions from the tanker is at least partially dependent on how far the cover is opened.

Another unloading procedure, of which there are numerous variations, is to pump the hot asphalt into a large open funnel which is connected to a surge tank. From the surge tanks, the asphalt is pumped directly into storage tanks. Emission sources under the surge tank configuration are the tanker, the interface between the tanker and the surge tank, the surge tank, and the storage tanks. The emissions from these sources are primarily organic particulate. The quantity of emissions depends on the asphalt temperature and on the asphalt characteristics.

Asphalt flux is usually stored at 51 to 79°C (124 to 174°F), although storage temperatures of up to 232°C (450°F) have been noted. The temperature is usually maintained with steam coils in the tanks at the lower temperatures. Oil- or gas-fired preheaters are used to maintain the asphalt flux at temperatures above 93°C (200°F).[121-123]

Asphalt is transferred within a roofing plant by closed pipeline. Barring leaks, the only potential emission sources are the end-points. These end-points are the storage tanks, the asphalt heaters (if not the closed tube type), and the air blowing stills.

Saturant and coating asphalts used to manufacture roofing materials are prepared by blowing air through tanks of hot asphalt flux. Saturant and coating asphalts are primarily distinguished by the differences in their softening points. The softening point of saturant asphalts is between 40 and 74°C (104 to 165°F), while coating asphalts soften at about 110°C (230°F). The configuration of a typical air blowing operation is shown in Figure 22.[121] This operation consists primarily of a blowing still which is a tank fitted near its base with a sparger. The purpose of the sparger is to increase contact between the blowing air and the asphalt. Air is forced through holes in the sparger into a tank of hot [204 to 243°C (400 to 470°F)] asphalt flux. The air rises through the asphalt and initiates an exothermic oxidation reaction. Oxidizing the asphalt has the effect of raising its softening temperature, reducing penetration, and modifying other characteristics. Catalysts are sometimes added to the asphalt flux during air blowing to better facilitate these transformations. The time required for air blowing of asphalt depends on a number of factors including the characteristics of the asphalt flux, the characteristics desired for the

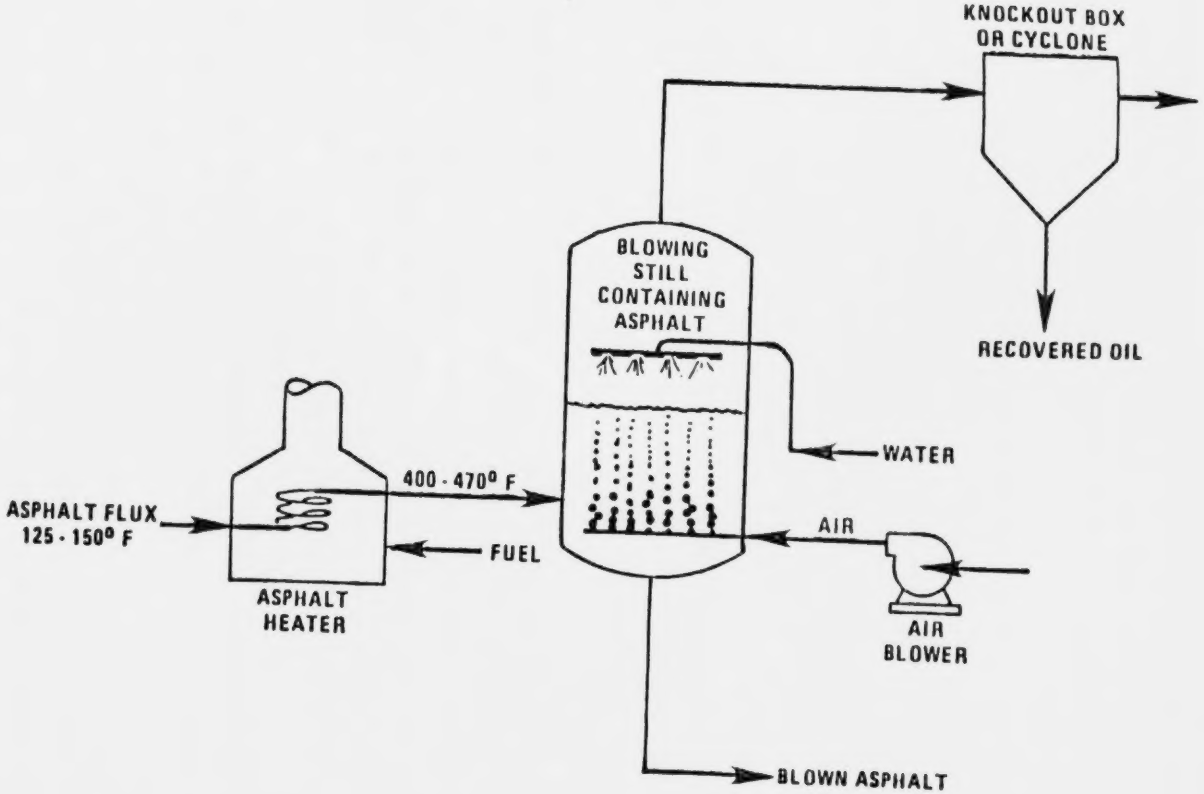

KNOCKOUT BOX
OR CYCLONE
RECOVERED OIL
BLOWING
STILL
CONTAINING
ASPHALT
WATER
AIR
AIR
BLOWER
ASPHALT FLUX
125 - 150° F
400 - 470° F
FUEL
ASPHALT
HEATER
BLOWN ASPHALT

Figure 22. Typical asphalt air blowing operation.[2]

finished product, the reaction temperature, the type of still used, the air injection rate, and the efficiency with which the air entering the still is dispersed throughout the asphalt. Blowing times may vary in duration from 30 minutes to 12 hours.[121]

Asphalt blowing is a highly temperature-dependent process, as the rate of oxidation increases rapidly with increases in temperature. Asphalt is preheated to 204 to 243°C (400 to 470°F) before blowing is initiated to assure that the oxidation process will start an an acceptable rate. Conversion does take place at lower temperatures but is much slower. Due to the exothermic nature of the reaction, the asphalt temperature rises as blowing proceeds. This, in turn, further increases the reaction rate. Asphalt temperature is normally kept at about 260°C (500°F) during blowing by spraying water onto the surface of the asphalt, although external cooling may also be used to remove the heat of reaction. The allowable upper limit to the reaction temperature is dictated by safety considerations, with the maximum temperature of the asphalt usually kept at least 28°C (50°F) below the flash point of the asphalt being blown.[121]

The design and location of the sparger in the blowing governs how much of the asphalt surface area is physically contacted by the injected air, and the vertical height of the still determines the time span of this contact. Vertical stills, because of their greater head (asphalt height) require less air flow for the same amount of asphalt-air contact. Both vertical and horizontal stills (see Figures 23 and 24) are used for asphalt blowing, but where new design is involved, a vertical type is preferred by the industry because of the increased asphalt-air contact and consequent reduction in blowing times.[121] Asphalt losses from vertical stills are also reported to be less than those from horizontal stills. All recent blowing still installations have been of the vertical type. Asphalt blowing can be either a batch process or a continuous operation; however, the majority of facilities use a batch process.

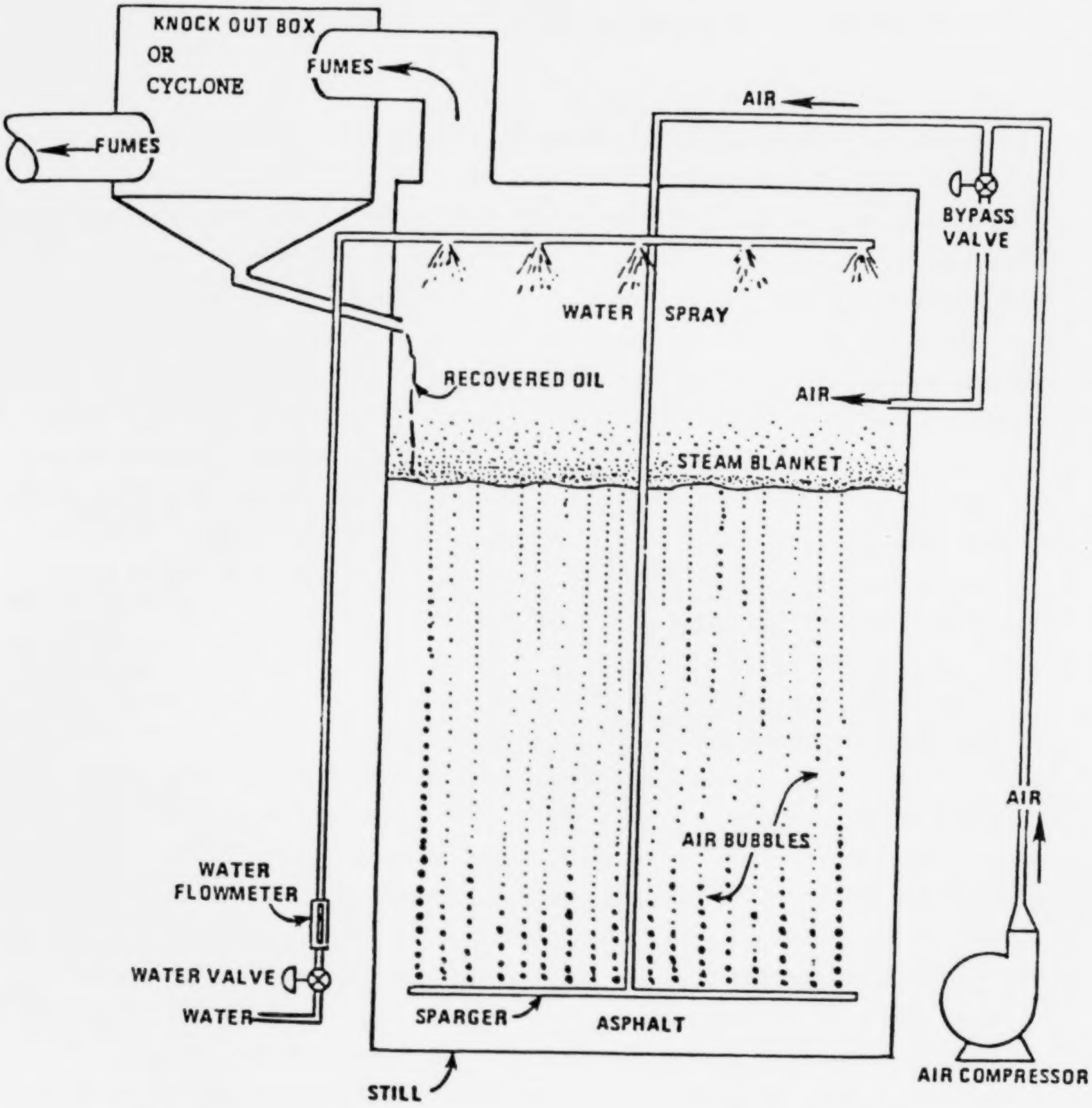

KNOCK OUT BOX
OR
CYCLONE
FUMES
FUMES
AIR
BYPASS VALVE
WATER
SPRAY
RECOVERED OIL
AIR
STEAM BLANKET
AIR
AIR BUBBLES
WATER FLOWMETER
WATER VALVE
WATER
SPARGER
ASPHALT
STILL
AIR COMPRESSOR

Figure 23. Typical configuration of a vertical asphalt air blowing still.[121]

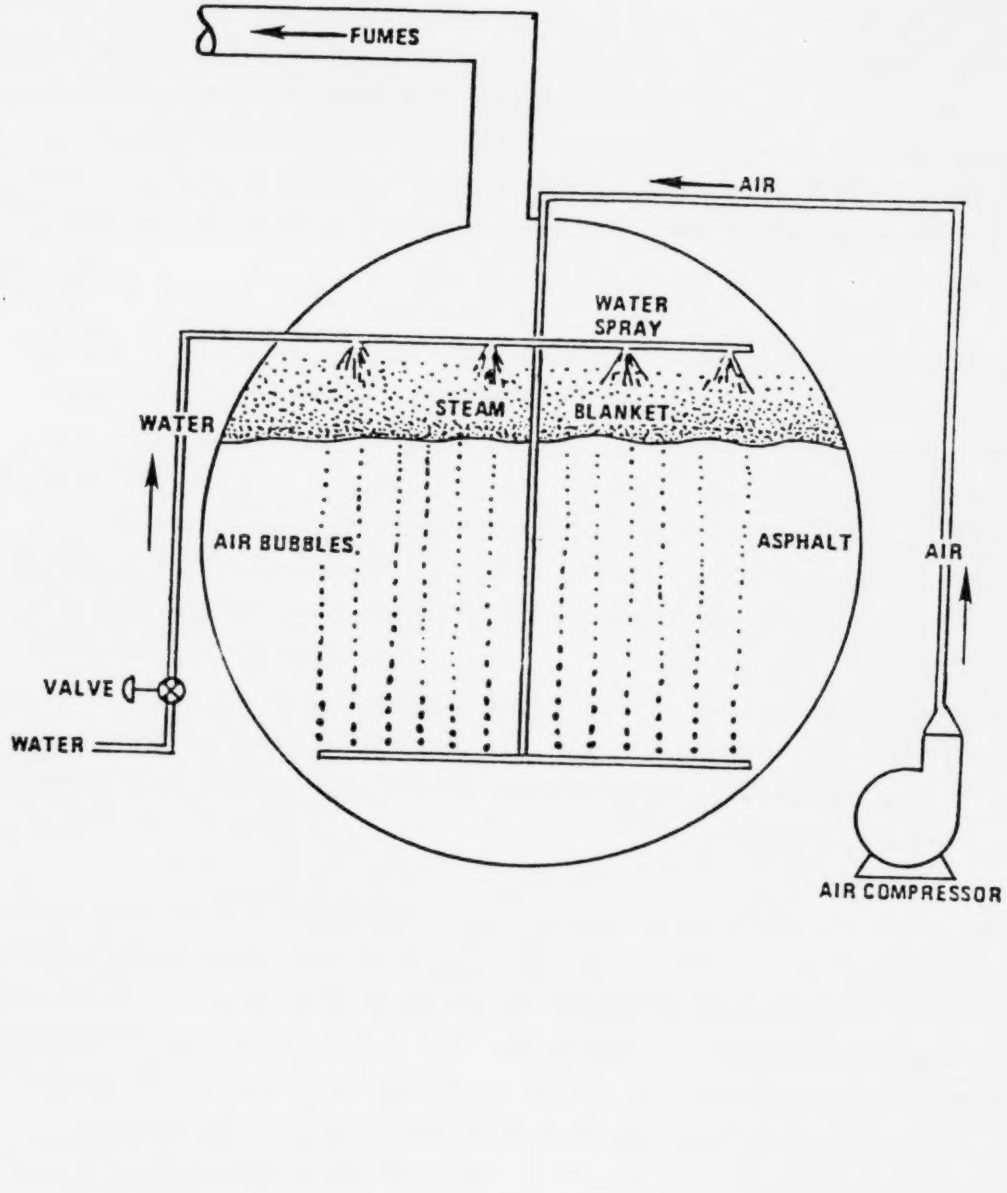

FUMES
AIR
WATER
SPRAY
STEAM
BLANKET
WATER
AIR BUBBLES
ASPHALT
AIR
VALVE
WATER
AIR COMPRESSOR

Figure 24. Typical configuration of a horizontal asphalt air blowing still.[121]

Blown asphalt (saturant and coating asphalt) is used to produce asphalt roofing and siding products according to the process depicted in Figure 25.[121] A roll of felt is installed on the felt reel and unwound onto a dry floating looper. The dry floating looper provides a reservoir of felt material to match the intermittent operation of the felt roller to the continuous operation of the line. Felt is unwound from the roll at a faster rate than is required by the line, with the excess being stored in the dry looper. The flow of felt to the line is kept constant by raising the top set of rollers and increasing looper capacity. The opposite action occurs when a new roll is being put on the felt reel and spliced in, and the felt supply ceases temporarily. There are no POM emissions generated in this processing step.[121]

Following the dry looper, the felt enters the saturator where moisture is driven out and the felt fibers and intervening spaces are filled with saturant asphalt. (If a fiberglass mat web is used instead of felt, the saturation step and the subsequent drying-in process are bypassed.) The saturator also contains a looper arrangement which is almost totally submerged in a tank of asphalt maintained at a temperature of 232 to 260°C (450 to 500°F). The absorbed asphalt increases the sheet or web weight by about 150 percent. At some plants, the felt is sprayed on one side with asphalt to drive out the moisture prior to dipping. This approach reportedly results in higher POM emissions than does use of the dip process alone.[121] The saturator is a significant POM emissions source within the asphalt roofing process.

The saturated felt then passes through drying-in drums and onto the wet looper, sometimes called the hot looper. The drying-in drums press surface saturant into the felt. Depending on the required final product, additional saturant may also be added at this point. The amount of absorption depends on the viscosity of the asphalt and the length of time the asphalt remains fluid. The wet looper increases absorption by providing time for the saturant asphalt to penetrate the felt. The wet looper operation has been

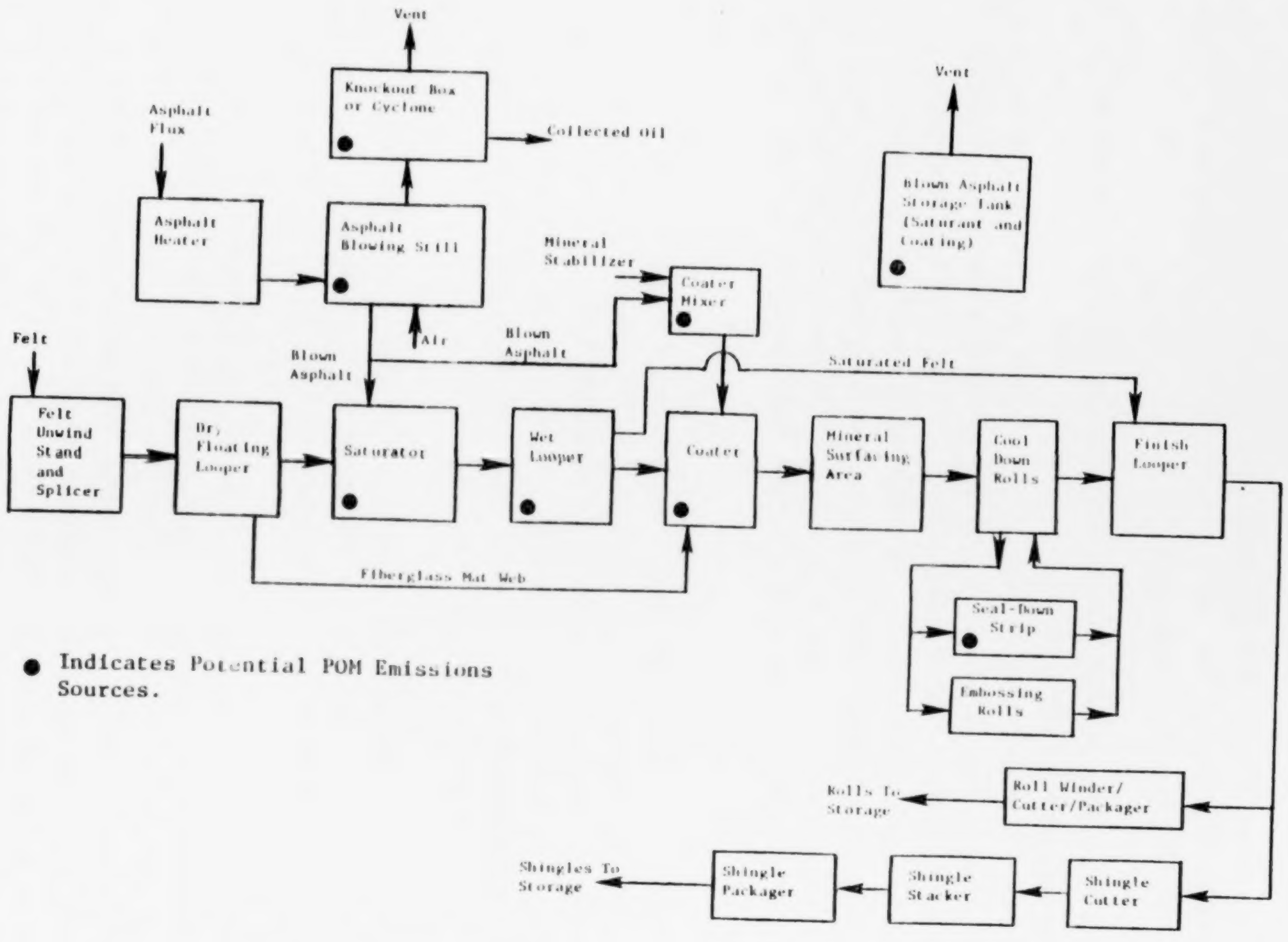

Vent
Knockout Box or Cyclone
Collected Oil
Asphalt Flux
Asphalt Heater
Asphalt Blowing Still
Vent
Blown Asphalt Storage Tank (Saturant and Coating)
Mineral Stabilizer
Coater Mixer
Air
Blown Asphalt
Blown Asphalt
Saturated Felt
Felt
Felt Unwind Stand and Splicer
Dry Floating Looper
Saturator
Wet Looper
Coater
Mineral Surfacing Area
Cool Down Rolls
Finish Looper
Fiberglass Mat Web
Seal-Down Strip
Embossing Rolls
● Indicates Potential POM Emissions Sources.
Rolls To Storage
Roll Winder/ Cutter/Packager
Shingles To Storage
Shingle Packager
Shingle Stacker
Shingle Cutter

Figure 25. Diagram of an asphalt roofing material manufacturing line.[121]

shown to be a significant source of organic particulate emissions within the asphalt roofing process. Although the wet looper is a potential source of POM emissions, their severity has not been defined.[121,122]

If saturated felt is being produced, the sheet bypasses the next two steps (coating and surfacing) and passes directly to the cool-down section. For surfaced roofing products, however, the saturated felt is carried to the coater station where a stabilized asphalt coating is applied to both the top and bottom surfaces. Stabilized coating contains a mineral stabilizer and a harder, more viscous coating asphalt which has a higher softening point than saturant asphalt. The coating asphalt and mineral stabilizer are mixed in approximately equal proportions. The mineral stabilizer may consist of finely divided lime, silica, slate dust, dolomite, or other mineral materials.

The weight of the finished product is controlled by the amount of coating used. The coater rollers can be moved closer together to reduce the amount of coating applied to the felt, or separated to increase it. Many modern plants are equipped with automatic scales which weigh the sheets in the process of manufacture and warn the coater operator when the product is running under or over specifications.

The coater is a significant emissions source within the roofing production process. It releases asphalt fumes containing organic particulate, some of which may be POM compounds.[121,122]

The function of the coater-mixer is to mix coating asphalt and a mineral stabilizer in approximately equal proportions. The stabilized asphalt is then piped to the coating pan. The asphalt is piped in at about 232 to 260°C (450 to 500°F), and the mineral stabilizer is delivered by screw conveyor. There is often a preheater immediately ahead of the coater-mixer to dry and preheat the material before it is fed into the coater-mixer. This eliminates moisture problems and also helps to maintain the temperature above 160°C (320°F) in the coater-mixer. The coater-mixer is usually covered or enclosed, with an exhaust pipe for the air displaced by (or carried with) the incoming materials. The coater-mixer is viewed as a potential source of POM emissions, but not a significant one.[121,122]

The next step in the production of coated roofing products is the application of mineral surfacing. The surfacing section of the roofing line usually consists of a multi-compartmented granule hopper, two parting agent hoppers, and two large press rollers. The hoppers are fed through flexible hoses from one or more machine bins above the line. These machine bins provide temporary storage and are sometimes called surge bins. The granule hopper drops colored granules from its various compartments onto the top surface of the moving sheet of coated felt in the sequence necessary to produce the desired color pattern on the roofing. This step is bypassed for smooth-surfaced products.[121]

Parting agents such as talc and sand (or some combination thereof) are applied to the top and back surfaces of the coated sheet from parting agent hoppers. These hoppers are usually of an open-topped, slot-type design, slightly longer than the coated sheet is wide, with a screw arrangement for distributing the parting agent uniformly throughout its length. The first hopper is positioned between the granule hopper and the first large press roller, and 0.2 to 0.3 m (8 to 12 in) above the sheet. It drops a generous amount of parting agent onto the top surface of the coated sheet and slightly over each edge. Collectors are often placed at the edges of the sheet to pick up this overspray, which is then recycled to the parting agent machine bin by open screw conveyor and bucket elevator. The second parting agent hopper is located between the rollers and dusts the back side of the coated sheet. Because of the steep angle of the sheet at this point, the average fall distance from the hopper to the sheet is usually somewhat greater than on the top side, and more of the material falls off the sheet.[121]

In a second technique used to apply backing agent to the back side of a coated sheet, a hinged trough holds the backing material against the coated sheet and only material that will adhere to the sheet is picked up. When the roofing line is not operating, the trough is tipped back so that no parting agent will escape past its lower lip.

Immediately after application of the surfacing material, the sheet passes through a cool-down section. Here the sheet is cooled rapidly by passing it around water-cooled rollers in an abbreviated looper arrangement. Usually, water is also sprayed on the surfaces of the sheet to speed the cooling process. The cool-down section is not a source of POM emissions.

Following cooling, self-sealing coated sheets usually have an asphalt seal-down strip applied. The strip is applied by a roller which is partially submerged in a pan of hot sealant asphalt. The pan is typically covered to minimize fugitive emissions. No seal-down strip is applied to standard shingle or roll goods products. Some products are also texturized at this point by passing the sheet over an embossing roll which forms a pattern in the surface of the coated sheet.[121]

The cooling process for both saturated sheets and coated sheets is completed in the next processing station known as the finish looper. In the finish looper, sheets are allowed to cool and dry gradually. Secondly, the finish looper provides line storage to match the continuous operation of the line to the intermittent operation of the roll winder. It also allows time for quick repairs or adjustments to the shingle cutter and stacker during continuous line operation or, conversely, allows cutting and packaging to continue when the line is down for repair. Usually, this part of the process is enclosed to keep the final cooling process from progressing too rapidly. Sometimes, in cold weather, heated air is also used to retard cooling. The finish looper is not viewed as a source of POM emissions.[121]

Following finishing, asphalt sheet destined for use in roll goods is wound on a mandrel, cut to the proper length, and packaged. When shingles are being made, the material from the finish looper is fed into the shingle cutting machine. After the shingles have been cut, they are moved by roller conveyor to manual or automatic packaging equipment. They are then stacked on pallets and transferred by fork lift to storage areas or waiting trucks.[121]

The primary POM emission sources associated with asphalt roofing are the asphalt air blowing stills (and associated oil knockout boxes) and the felt saturators.[122,124] Additional potential POM emission sources that have been identified include the wet looper, the coater-mixer, the felt coater, the seal-down stripper, and air blown asphalt storage tanks. Minor fugitive emissions are also possible from asphalt flux and blown asphalt handling and transfer operations.[121-124]

Process selection and control of process parameters reportedly can be used to minimize uncontrolled emissions, including POM, from asphalt air blowing stills, asphalt saturators, wet loopers, and coaters. Process controls include the use of the following:[121]

- dip saturators, rather than spray or spray-dip saturators;
- vertical stills, rather than horizontal stills;
- asphalts that inherently produce low emissions;
- higher flash point asphalts;
- reduced temperatures in the asphalt saturant pan;
- reduced asphalt storage temperatures; and
- lower asphalt blowing temperatures.

Dip saturators have been selected for most new asphalt roofing line installations in recent years, and this trend is expected to continue. Recent asphalt blowing still installations have been almost exclusively of the vertical type because of its higher efficiency and lower emissions. Vertical stills occupy less space and require no heating during oxidizing [if the temperature of the incoming flux is above 204°C (400°F)]. Vertical stills are expected to be used in new installations equipped with stills and in most retrofit situations.[121]

Asphalt fluxes with lower flash points and softening points tend to have higher hydrocarbon emissions because these fluxes generally have been less severely cracked and contain more low-boiling fractions. Many of these light ends can be expected to boil off during blowing. Limiting the minimum softening and flash points of asphalt flux should reduce the amount of POM-containing fumes generated during blowing since less blowing is required to produce a saturant or coating asphalt. Saturant and coating asphalts with high softening points should reduce POM emissions from felt saturation and coating operations. However, producing the higher softening asphalt flux requires more blowing, which increases uncontrolled emissions from the blowing operation.[121]

Although these process-oriented emission control measures are useful, emissions capture equipment and add-on emissions control equipment are also necessary in asphalt roofing material production facilities. The capture of potential POM emissions from asphalt blowing stills, asphalt storage tanks, asphalt tank truck unloading, and the coater-mixer can and is being achieved in the industry by the use of enclosure systems around the emission operations. The enclosures are maintained under negative pressure and the contained emissions are ducted to the controls specified in Table 55.[121] Potential emissions from the saturator, wet looper, and coater are generally collected by a single enclosure, by a canopy type hood, or by an enclosure/hood combination. Typically applied controls for POM emission sources in asphalt roofing plants are summarized in Table 55.

Emission Factors

For the asphalt roofing manufacturing industry, POM emission factor data exist for asphalt air blowing stills and for asphalt saturators. The available information is presented in Table 56.[121-124] As might be expected, the quantitative results are highly variable. However, qualitatively the POM compounds identified in the emission streams are very consistent.

TABLE 55. CONTROL DEVICES USED ON POM EMISSION SOURCES IN ASPHALT ROOFING PLANTS[121]

Emission Source	Control Device
A. Saturator, wet looper (hot looper), and coater[a]	Afterburner High velocity air filter Electrostatic precipitator
B. Coater-mixer[b]	High velocity air filter
C. Asphalt blowing still	Afterburner
D. Asphalt storage tanks[c]	Mist eliminator

[a] These sources usually share a common enclosure, and emissions are ducted to a common control device.

[b] Emissions from the coater-mixer are controlled, at some plants, by routing fumes to the control device used for sources listed in A, above.

[c] Some plants control emissions from storage tanks with the same device used for processes listed in A and then use a mist eliminator during periods when the roofing line is not operating (e.g., weekends). Asphalt delivery can be accomplished via a closed system which vents emissions to the same control device as that used for the tanks.

TABLE 56. SUMMARY OF POM EMISSION FACTOR DATA FOR SOURCES IN ASPHALT ROOFING MATERIAL PLANTS

Emission Source	Control Device	Uncontrolled Total POM Emission Factor,[a] g/Mg (lb/ton)	Controlled Total POM Emission Factor,[a] g/Mg (lb/ton)	Percent POM Control	Reference
Saturator	ESP	0.21 (0.00042)[c,d]	0.096 (0.00019)[c,e]	54.1	121[b]
Saturator	Afterburner	0.33 (0.00066)[f,g]	0.63 (0.0013)[c,h]	---	121[b]
Saturator and Asphalt Storage Tanks (vented to same control device)	High Velocity Air Filter	2.1 (0.0042)[i,j]	0.19 (0.00038)[k,l]	91.1	121[b]
Asphalt Blowing Still	Afterburner	15.2 (0.030)[c,m]	0.048 (0.0001)[c,n]	99.7	121[b]
Asphalt Blowing Still	Fume Incinerator	---	0.0021 (4.2×10^{-6})[o]	---	122[p]
Saturator	High Efficiency Air Filter/ Fume Incinerator	---	0.0043 (8.0×10^{-6})[q]	---	122[p]
Saturator	None	0.001 - 0.008 (2.0×10^{-6} - 1.6×10^{-5})[r,s]	---	---	124
Saturator	None	0.005 - 0.008 (1.0×10^{-5} - 1.6×10^{-5})[r,s]	---	---	124
Saturator	High Efficiency Air Filter	---	0.003 (6.0×10^{-6})[r,s]	---	124
Saturator	Afterburner	---	0.001 (2.0×10^{-6})[r,s]	---	124
Saturator	High Efficiency Air Filter	---	0.001 (2.0×10^{-6})[r,s]	---	124
Saturator	Afterburner	---	0.05 (1.0×10^{-4})[r,s]	---	124
Asphalt Blowing Still	None	0.0048 - 4.1 (9.6×10^{-6} - 0.0082)[r,s]	---	---	124
Asphalt Blowing Still	Process Heater Furnace	---	0.0024 - 0.0093 (4.8×10^{-6} - 1.9×10^{-5})[r,s]	---	124
Asphalt Blowing Still	Stack Baffles	---	4.8 (0.0096)[s]	---	124, 125

[a] Saturator emission factors are expressed in terms of mass of POM emitted per mass of asphalt roofing (e.g., shingles, rolls) produced. Asphalt blowing still emission factors are expressed in terms mass of POM emitted per mass of asphalt blown.

[b] All data in Reference 121 were obtained using EPA Method 26 and a POM collection column developed by Battelle-Columbus laboratory.

[c] Anthracene, phenanthrene, methyl anthracenes, fluoranthene, pyrene, methyl pyrene, benz(c)phenanthrene, chrysene, benz(a)anthracene, methyl chrysenes, benzo fluoranthenes, benzo(a)pyrene, and benzo(e)pyrene were detected in these emissions.

[d] Methyl anthracenes constituted 62 percent, anthracene/phenanthrene 17 percent, and methyl chrysenes 7 percent of total POM emissions.

TABLE 56. SUMMARY OF POM EMISSION FACTOR DATA FOR SOURCES IN ASPHALT ROOFING MATERIAL PLANTS (Continued)

---

[e] Methyl anthracenes constituted 57 percent, anthracene/phenanthrene 25 percent, and methyl pyrene/fluoranthene 12 percent of total POM.

[f] The POM compounds given in footnote c and perylene were detected in these emissions.

[g] Methyl anthracenes constituted 59 percent, anthracene/phenanthrene 27 percent, and methyl pyrene/fluoranthene 8 percent of total POM.

[h] Methyl anthracenes constituted 45 percent, anthracene/phenanthrene 27 percent, methyl chrysenes 10 percent, and chrysene/benz(a)anthracene 9 percent of total POM.

[i] The POM compounds given in footnote c and perylene and 3-methylcholanthrene were detected in these emissions.

[j] Methyl anthracenes constituted 54 percent, anthracene/phenanthrene 21 percent, and methyl pyrene/fluoranthene 10 percent of total POM.

[k] Anthracene, phenanthrene, methyl anthracenes, fluoranthene, pyrene, methyl pyrene, benzo fluoranthenes, chrysene, benz(a)anthracene, methyl chrysenes, benzo(a)pyrene, and benzo(e)pyrene were detected in these emissions.

[l] Methyl anthracenes constituted 47 percent, anthracene/phenanthrene 34 percent, and methyl pyrene/fluoranthene 15 percent of total POM.

[m] Methyl anthracenes constituted 44 percent, methyl pyrene/fluoranthene 17 percent, anthracene/phenanthrene 16 percent, and methyl chrysenes 15 percent of total POM.

[n] Anthracene/phenanthrene constituted 34 percent, methyl anthracenes 30 percent, and methyl pyrene/fluoranthene 22 percent of total POM.

[o] Value represents the measured average from two facilities. Each still was controlled by a fume incinerator. One incinerator reduced POM emissions by 80 percent; however, in the other POM emissions increased by a factor of two. Benz(c)phenanthrene, 7,12-dimethyl(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, 3-methylcholanthrene, dibenz(a,h)pyrene, and dibenz(a,i)pyrene were identified in the emissions.

[p] Data reported in Reference 122 were obtained using a Method 5 sampling train modified by placing the filter after the impinger series. Analysis was accomplished using GC/MS.

[q] Value represents the measured average from two facilities, one controlled by a high efficiency air filter and one controlled by a fume incinerator. The air filter reportedly reduced POM emissions by 70 percent, while the fume incinerator had no effect on POM emissions.

[r] Total POM value reported for samples collected by EPA Method 5 or a modification and analyzed for benz(c)phenanthrene, 7,12-dimethylbenz(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, 3-methylcholanthrene, dibenz(a,h)pyrene, dibenz(a,i)pyrene using GC/MS.

[s] Value represents results of total particulate POM analysis. Vaporous POM were not collected and analyzed.

NOTE: A dash indicates that those data are not available or the data are not applicable.

Uncontrolled total POM emissions from asphalt saturators ranged from 0.001 to 2.1 g/Mg (2.0 x 10^{-6} to 0.0042 lb/ton).[121,124] The values reported in Reference 124 are much less than those in Reference 121 because few, if any, vaporous POM emissions were collected by the sampling procedure used in Reference 124. The sampling procedure used for the Reference 121 samples apparently was more successful for condensing and collecting vaporous POM. The same situation exists in the asphalt blowing still results where the total POM range is 0.0048 to 15.2 g/Mg (9.6 x 10^{-6} to 0.030 lb/ton).[121,122,124,125] The problem persists with the controlled emission factors where the total POM factors for afterburner-controlled saturators range from 0.001 to 0.63 g/Mg (2.0 x 10^{-6} to 0.0013 lb/ton) and the factors for incineration-controlled blowing stills range from 0.0021 to 0.048 g/Mg (4.2 x 10^{-6} to 0.001 lb/ton).[121,122,124] Because of the differing sampling and analysis procedures used to obtain the factors given in Table 56, data comparisons between sources is difficult and could lead to erroneous conclusions.

The POM compounds identified in roofing source emissions were consistent within a source type (e.g., saturators) and between different source types. Anthracene/phenanthrene, methyl anthracenes, fluoranthene, pyrene, methyl pyrene, chrysene, benz(a)anthracene, methyl chrysenes, benzo fluoranthenes, benzo(a)pyrene, and benzo(e)pyrene were identified in the emission measurements of practically every source. In both controlled and uncontrolled emissions of saturators and blowing stills, methyl anthracenes predominated. Anthracene/phenanthrene and methyl pyrene/fluoranthene also repeatedly constituted significant portions of total POM emissions. Generally, the three POM compound groups constituted between 90 and 95 percent of total POM measured.

Source Locations

As of mid-1986, there were 94 asphalt roofing manufacturing plants operating in the United States. A list of all current facilities as identified by the Asphalt Roofing Manufacturers Association, is provided in

Table 57.[126] States containing a relatively significant number of roofing plants include California, Texas, Ohio, and Alabama. These four States contain approximately 40 percent of the total number of roofing facilities. The majority of all plants nationwide are located in urban as opposed to rural areas.

HOT MIX ASPHALT PRODUCTION

Process Description

In the production of hot mix asphalt (also known as asphalt concrete), aggregate, which is composed of gravel, sand, and mineral filler, is heated to eliminate moisture and then mixed with hot asphalt cement. The resulting hot mixture is pliable and able to be compacted and smoothed. When it cools and hardens, hot mix asphalt provides a waterproof and durable pavement for roads, driveways, parking lots, and runways.

Currently, there are three types of hot mix asphalt plants in use in the United States: batch-mix, continuous-mix, and drum-mix. Batch-mix and continuous-mix plants separate the aggregate drying process from the mixing of aggregate with asphalt cement. Drum-mix plants combine these two processes. Production capacities for all three types of plants range from 36 to 544 Mg (40 to 600 tons) of hot mix per hour. The production capacity distribution for the three types of hot mix asphalt plants is presented in Table 58.[127] Over 80 percent of all hot mix asphalt production plants are mobile.[127]

Raw Materials--

The basic raw material of hot mix asphalt, aggregate, consists of any hard, inert mineral material mixed with a binding agent to produce hot mix asphalt. Aggregate typically comprises between 90 and 95 percent by weight of the asphalt mixture. Since aggregate provides most of the load-bearing properties of a pavement, the performance of the pavement depends on selection of the proper aggregate.[127]

TABLE 57. ASPHALT ROOFING MANUFACTURING LOCATIONS IN THE UNITED STATES IN 1986[126]

Company	Plant Locations
American Roofing Corporation	Chicago, IL
Bird, Incorporated	Norwood, MA
Celotex Corporation	Camden, AR Fremont, CA Fairfield, AL Russellville, AL Goldsboro, NC Los Angeles, CA Houston, TX Lockland, OH Perth Amboy, NJ San Antonio, TX Memphis, TN
Certainteed Corporation	Avery, OH Oxford, NC Shakopee, MN Savannah, GA
Consolidated Fiberglass Products	Bakersfield, CA
Dibiten, U. S. A.	South Gate, CA
Elk Corporation of America	Ennis, TX Tuscaloosa, AL
Evanite/Permaglas, Incorporated	Corvallis, OR
GAF Corporation	Baltimore, MD Dallas, TX Erie, PA Fontana, CA Millis, MA Minneapolis, MN Mobile, AL Mount Vernon, IN Savannah, GA Tampa, FL Chester, SC
The Garland Company	Cleveland, OH

TABLE 57. ASPHALT ROOFING MANUFACTURING LOCATIONS IN THE UNITED STATES IN 1986[126] (Continued)

Company	Plant Locations
Georgia-Pacific Corporation	Ardmore, OK Daingerfield, TX Franklin, OH Hampton, GA Quakertown, PA Denver, CO Pryor, OK
Globe Industries, Incorporated	Whiting, IN
Iko Industries Limited	Wilmington, DE Chicago, IL Franklin, OH
Koppers Company	Chicago, IL Fontana, CA Houston, TX Wickliffe, OH Woodward, AL Youngstown, OH
Leatherback Industries	Albequerque, NM Hollister, CA Auburn, WA
Lunday-Thagard	South Gate, CA
Manville Corporation	Fort Worth, TX Manville, NJ Pittsburg, CA Savannah, GA Waukegan, IL Etowan, TN Waterville, OH
Nord Bitumi U. S., Incorporated	Plattsburgh, NY Macon, GA
Owens-Corning Fiberglas Corporation	Atlanta, GA Brookville, IN Compton, CA Denver, CO

TABLE 57. ASPHALT ROOFING MANUFACTURING LOCATIONS IN THE UNITED STATES IN 1986[126] (Continued)

Company	Plant Locations
Owens-Corning Fiberglas Corporation (continued)	Houston, TX Irving, TX Jacksonville, FL Jessup, MD Kearny, NJ Medina, OH Memphis, TN Minneapolis, MN Morehead City, NC Oklahoma City, OK Portland, OR Summit, IL Aiken, SC Barrington, NJ Kansas City, MO
Siplast, Incorporated	Arkadelphia, AK
Tamko Asphalt Products, Incorporated	Joplin, MO Frederick, MD Phillipsburg, KS Tuscaloosa, AL Knoxville, TN
Tremco, Incorporated	Cleveland, OH
U. S. Intec, Incorporated	Port Arthur, TX North Branch, NJ Stockton, CA
W. R. Grace and Company	Cambridge, MA

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

TABLE 58. PRODUCTION CAPACITY DISTRIBUTION FOR BATCH, CONTINUOUS, AND DRUM-MIX HOT MIX ASPHALT PLANTS[127]

Type of Plant	Production Range, Mg/h (tons/h)	Percentage of Plants Within Production Range
Batch-mix Plants	Under 136 (Under 150)	25
	136 - 272 (150 - 300)	63
	273 - 363 (301 - 400)	11
	Over 363 (Over 400)	1
		100
Drum-mix Plants	Under 136 (Under 150)	15
	136 - 272 (150 - 300)	52
	273 - 363 (301 - 400)	26
	Over 363 (Over 400)	7
		100
Continuous-mix Plants	Under 136 (Under 150)	43
	136 - 272 (150 - 300)	21
	273 - 363 (301 - 400)	19
	Over 363 (Over 400)	17
		100

Asphalt cement is used as the binding agent for aggregate. It prevents moisture from penetrating the aggregate and it acts as a cushioning agent. Typically, asphalt cement constitutes 4 to 6 percent by weight of a hot mix asphalt mixture.[127]

Asphalt cement is generated as a residue from the distillation of crude petroleum. It is classified into grades under one of three systems. The most commonly used system classifies asphalt cement based on its viscosity at 60°C (140°F). The more viscous the asphalt cement, the higher its numerical rating. An asphalt cement of grade AC-40 is considered a hard asphalt [i.e., a viscosity of 4000 grams per centimeter per second (g/cm-s) (poises)], while an asphalt cement of grade AC-2.5 is considered a soft asphalt [i.e., a viscosity of 250 g/cm-s (poises)]. Several western States use a second grading system that measures viscosity of the asphalt cement after a standard simulated aging period. This simulated aging period consists of exposure to a temperature of 163°C (325°F) for 5 hours. Viscosity is measured at 60°C (140°F), with grades ranging from AR-1000 for a soft asphalt cement [1000 g/cm-s (poises)] to AR-16000 for a hard asphalt cement [16,000 g/cm-s (poises)]. A third grading system is based on the penetration allowed by the asphalt cement. Grade designation 40 to 50 means that a needle with a weight attached will penetrate the asphalt cement between 40 and 50 tenths of a millimeter under standard test conditions. The hard asphalt cements have penetration ratings of 40 to 50, while the soft grades have penetration ratings of 200 to 300.[127]

The asphalt cement grade selected for different hot mix asphalts depends on the type of pavement, climate, and type and amount of traffic expected. Generally, asphalt pavement bearing heavy traffic in warm climates would require a harder asphalt cement than pavement subject to either light traffic or cold climate conditions.

Another material that may be used in the production of new or virgin hot mix asphalt is recycled hot mix asphalt (RAP) which is pavement material that has been removed from existing roadways. Recycled hot mix asphalt is used by a growing number of companies in their hot mix asphalt mixtures. The Surface Transportation Assistance Act of 1982 encourages recycling by providing a 5 percent increase in Federal funds to State agencies that recycle asphalt concrete pavement. Rarely does the recycled hot mix asphalt comprise more than 60 percent by weight of the new asphalt mixture. Twenty-five percent recycled hot mix asphalt mixtures are typical in batch plants while 40 to 50 percent RAP mixtures are typical in drum-mix plants.[127]

Rejuvenating agents are sometimes used in recycled hot mix asphalts to bring the weathered and aged asphalt cement in the recycled mixture up to the specifications of the new asphalt mixture. Usually, a soft asphalt cement, a specially prepared high viscosity oil, or a hard asphalt cement blended with a low viscosity oil are used as rejuvenating agents. The amount of rejuvenating agent added depends on the properties of the recycled asphalt and on the specifications for the hot mix asphalt product.

Sulfur has also been used on an experimental basis as a substitute for a portion of the asphalt cement in hot mix asphalt mixtures. Tests have shown that the asphalt cement/sulfur combination is better able to bind with aggregate than is asphalt cement alone. Hot mix asphalt pavements containing the asphalt cement/sulfur combination appear to be stronger and less susceptible to temperature changes than those containing asphalt cement alone.

The use of sulfur is not competitive with asphalt cement in asphalt concrete mixes for several reasons, including environmental questions, worker objections (odor), and corrosion, all of which result from emissions of hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and elemental sulfur (S). In addition, sulfur is almost twice as dense as asphalt cement. Consequently, to make the use of sulfur economically feasible, the cost of sulfur must be less than half the cost of asphalt cement.[127]

Batch-Mix Plants--

The primary processes of a typical batch-mix hot mix asphalt facility are illustrated in Figure 26.[127] Aggregate of various sizes is stockpiled at the plant for easy access. The moisture content of the stockpiled aggregate usually ranges from 3 to 5 percent. The moisture content of recycled hot mix asphalt typically ranges from 2 to 3 percent. The different sizes of aggregate are typically transported by front-end loader to separate cold feed bins and metered onto a feeder conveyor belt through gates at the bottom of the bins. The aggregate is screened before it is fed to the dryer to keep oversized material out of the mix.

The screened aggregate is then fed to a rotating dryer with a burner at its lower (discharge) end that is fired with fuel oil, natural gas, or propane. The dryer removes moisture from the aggregate and heats the aggregate to the proper mix temperature. Inside the dryer are longitudinal flights (metal slats) that lift and tumble the aggregate, causing a curtain of material to be exposed to the heated gas stream. This curtain of material provides greater heat transfer to the aggregate than would occur if the aggregate tumbled along the bottom of the drum towards the discharge end. Aggregate temperature at the discharge end of the dryer is about 149°C (300°F). The amount of aggregate that a dryer can heat depends on the size of the drum, the size of the burner, and the moisture content of the aggregate. As the amount of moisture to be removed from the aggregate increases, the effective production capacity of the dryer decreases.

Vibrating screens segregate the heated aggregate into bins according to size. A weigh hopper meters the desired amount of the various sizes of aggregate into a pugmill mixer. The pugmill typically mixes the aggregate for approximately 15 seconds before hot asphalt cement from a heated tank is sprayed into the pugmill. The pugmill thoroughly mixes the aggregate and hot asphalt cement for 25 to 60 seconds. The finished hot mix asphalt is either directly loaded into trucks or held in insulated and/or heated

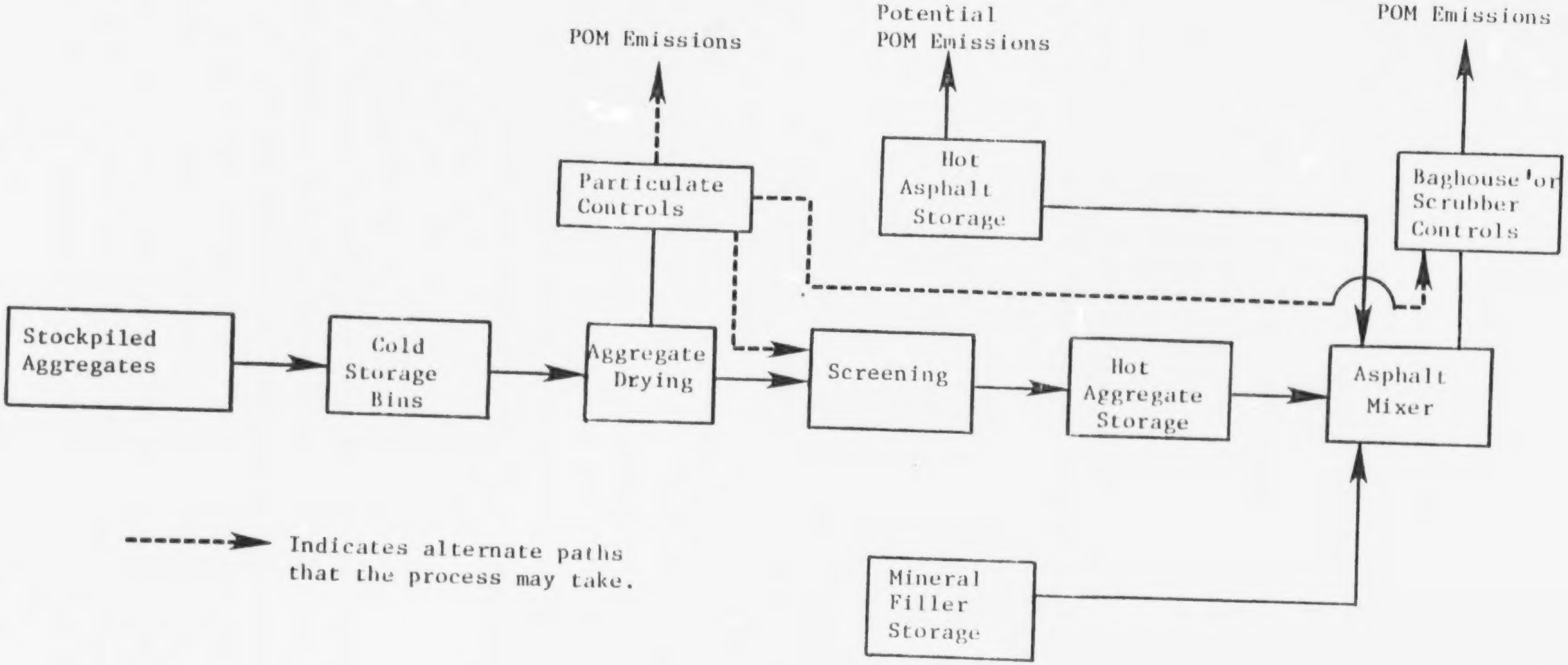

POM Emissions
Potential
POM Emissions
POM Emissions
Particulate Controls
Hot Asphalt Storage
Baghouse or Scrubber Controls
Stockpiled Aggregates
Cold Storage Bins
Aggregate Drying
Screening
Hot Aggregate Storage
Asphalt Mixer
Mineral Filler Storage
Indicates alternate paths that the process may take.

Figure 26. Typical process used in a batch-mix hot mix asphalt plant.[127]

storage silos. Depending on the production specifications, the temperature of the hot mix asphalt product mix can range from 107 to 177°C (225 to 350°F) at the end of the production process.

When mix containing recycled asphalt is produced, the aggregate is superheated (compared to totally virgin hot mix production) to about 315°C (600°F) to ensure sufficient heat transfer to the recycled asphalt when it is mixed with the virgin materials. Recycled hot mix asphalt may be added either to the pugmill mixer or at the discharge end of the dryer. Rarely is more than 30 percent recycled asphalt used in batch plants for the production of hot mix asphalt.

Continuous-Mix Plants--

Continuous-mix plants are very similar in configuration to batch plants. Continuous-mix plants have smaller hot bins (for holding the heated aggregate) than do batch plants. Little surge capacity is required of these bins because the aggregate is continuously metered and transported to the mixer inlet by a conveyor belt. Asphalt cement is continuously added to the aggregate at the inlet of the mixer. The aggregate and asphalt cement are mixed by the action of rotating paddles while being conveyed through the mixer. An adjustable dam at the outlet end of the mixer regulates the mixing time and also provides some surge capacity. The finished mix is transported by a conveyor belt to either a storage silo or surge bin.[127]

Drum-Mix Plants--

The essential components of a typical virgin hot mix asphalt drum-mix plant are shown in Figure 27.[127] Drum-mix plants dry the aggregate and mix it with the asphalt cement in the same drum, eliminating the need for the extra conveyor belt, hot bins and screens, weigh hopper, and pugmill. Although the drum of a drum-mix plant is much like the dryer of a batch plant, the burner is at the aggregate feed end rather than at the aggregate discharge end. The veil of aggregate is heated as it flows with the heated gas stream instead of countercurrent to the gas stream as in a batch plant.

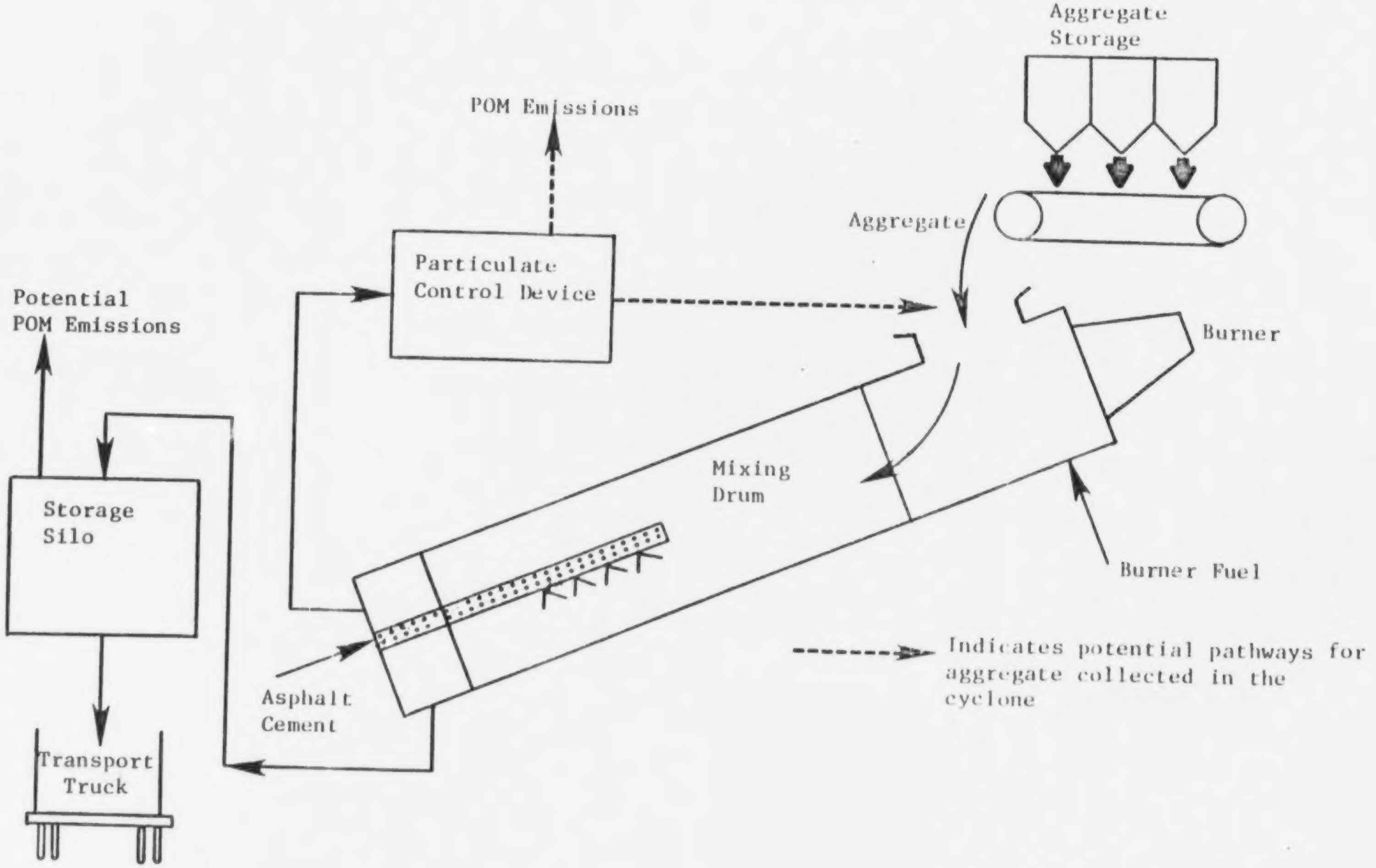

Aggregate
Storage
POM Emissions
Aggregate
Particulate
Control Device
Potential
POM Emissions
Burner
Mixing
Drum
Storage
Silo
Burner Fuel
Indicates potential pathways for aggregate collected in the cyclone
Asphalt
Cement
Transport
Truck

Figure 27. Typical drum-mix hot mix asphalt process.[127]

The burner in a drum-mix plant emits a much bushier flame than does the burner in a batch plant. The bushier flame is designed to provide earlier and greater exposure of the virgin aggregate to the heat of the flame. This design also protects the asphalt cement, which is injected approximately two-thirds of the way down the length of the drum, away from the direct heat of the flame. Drum-mix plants typically have more flights in their drums than do batch dryers to increase veiling of the aggregate and to improve overall heat transfer. The asphalt cement, which is usually injected from a pipe inserted from the discharge end of the rotating drum, coats the aggregate. The temperature of the mix as it leaves the drum usually ranges from 107 to 177°C (225 to 350°F). The hot mix asphalt is then transported by conveyor to a surge bin or to an insulated, and possibly heated, storage silo for truck load-out.

Recycled hot mix asphalt can also be used as a raw material in drum-mix plants. Currently in drum-mix plants, recycled hot mix asphalt is introduced through a collar midway down the drum and is dried by both the superheated aggregate and by the gas stream. The veil of virgin aggregate created by the flights in the drum keeps the high heat of the burner flame from reaching the recycled asphalt. Two vendors have attempted to improve on this approach by also expanding the drum diameter at the burner end to allow a shorter, bushier flame and to obtain more efficient heat transfer from the burner flame to the virgin aggregate.

One major advantage of drum-mix plants is that they can produce material containing higher percentages of recycled hot mix asphalt than batch plants can produce. With the greater veiling of aggregate, drum-mix plants are more efficient than batch plants at transferring heat and achieving proper mixing of recycled asphalt and virgin materials. The trend in hot mix asphalt production is towards drum-mix plants.[128]

Indirect Heated Plants--

A potential new commercial production process for hot mix asphalt involves indirect heating of the aggregate and asphalt cement in a mixer. In this process, asphalt cement and preheated aggregate are introduced through air-locks into a heated, sealed mixing unit. Synthetic heat transfer fluids are heated to 316 to 343°C (600 to 650°F) by a fuel efficient diesel- or gas-fired burner. These synthetic fluids heat the mixing unit chamber to approximately 149°C (300°F). Steam from the moisture driven off from the aggregate is piped to the cold feed bins to preheat the virgin aggregate. This preheating of the aggregate decreases energy costs for drying. The product hot mix asphalt is transported by an enclosed conveyor from the mixing unit to a storage silo. Because this process is sealed, there are no mixer process air emissions. The steam from the mixing unit condenses as it preheats the cold feed bins. The only other process emissions are the gases from the heater unit.

The indirect heated process has been successfully demonstrated with a pilot-scale plant capable of producing 14 to 18 Mg (15 to 20 tons)/hour of hot mix asphalt. Stationary and portable indirect heated plants have been designed with production capacities ranging from 45 to 204 Mg (50 to 225 tons)/hour, and commercial plants of 181 to 272 Mg (200 to 300 tons)/hour production capacity are expected by 1986.[127]

Polycyclic organic matter emissions in hot mix asphalt plants occur from the aggregate rotary dryers (due to fuel combustion) and from the hot mix asphalt mixing vessels (due to heating of the organics-containing asphalt materials). Most plants employ some form of mechanical collection, typically cyclones, to collect aggregate particle emissions from the rotary dryers. These cyclones would have a minimal collection efficiency for POM compounds because the POMs are either in vapor form or would predominantly exist on fine particles not captured by the cyclones. In many installations, the recovered aggregate is recycled to the hot mix asphalt process.

Overall, particulate matter emissions from hot mix asphalt mixers are controlled by wet scrubbers or baghouses.[127] Again, their success on POM emissions is dependent on the form of the POMs (i.e., vapor versus particulate and fine versus coarse particle). In some installations, the exhaust stream of the rotary dryer cyclones is vented to the baghouse or scrubber used for mixer emissions control.[129,130] One reference has indicated that for hot mix asphalt plants venting dry emissions to the mixer control device, the POM compounds detected in the mixer control device emissions were predominantly a function of the rotary dryer and not the mixer.[130]

Because the drum-mix hot mix asphalt process is based on a parallel flow design (i.e., hot gases and aggregate flow through the dryer in the same direction), general particulate matter emissions from this process are less than from a conventional batch process. However, because the asphalt materials contained in the process are heated to a higher temperature for a longer time, the drum-mix process potentially may produce greater levels of POM emissions.[128]

In any of the processes used to produce hot mix asphalt, fugitive POM emissions may occur due to evaporative losses from asphalt handling and storage. Emissions of this type would be highly variable. No examination of fugitive POM emissions from hot mix asphalt plants could be found in the literature.

Emission Factors

Several total POM and speciated POM emission factors were identified in the literature for hot mix asphalt production facilities. A summary of these factors for total POM is presented in Table 59.[128-132] The limited data in Table 59 indicate that drum-mix plants potentially have greater POM emissions than batch plants and plants using recycled hot mix asphalt have higher POM emissions than those employing only virgin materials.

TABLE 59. POM EMISSION FACTORS FOR HOT MIX ASPHALT PLANTS

Data Reference	Plant Type	Asphalt Feed Type	Contents	Total POM Emission Factor (mg POM/Mg Asphalt Produced)
128	Batch	Virgin	Cyclone followed by Wet Scrubber	13.0
129	Batch	Virgin	Cyclone followed by Wet Scrubber	19.7[a]
130, 131	Batch	Virgin	Cyclone	9.5[b]
130, 131	Batch	Virgin	Cyclone followed by Spray Tower	4.1[c]
132	Drum-Mix	Virgin	Knockout Box	22.1[d]
132	Drum-Mix	Virgin	Knockout Box followed by Venturi Scrubber	13.5[e]
132	Drum-Mix	Recycled and Virgin	Knockout Box	35.9[f]
132	Drum-Mix	Recycled and Virgin	Knockout Box followed by Venturi Scrubber	16.9[g]

[a] Almost 75 percent of this total consists of dibenzothiopene, anthracene, phenanthrene, and methylanthracenes. Benzo(a)pyrene constitutes less than 1.5 percent of the total. In the emission test at this source, 90 percent of the POM emissions were identified as particulate POM and 10 percent as gaseous POM.

[b] Benzo(a)pyrene constitutes 7.3 percent of this total.

[c] Benzo(a)pyrene constitutes less than 1.5 percent of this total.

[d] Approximately 92 percent of this total consists of phenanthrene (61 percent), pyrene (16 percent), anthracene (9 percent), and fluoranthene (6 percent). Benzo(a)pyrene accounts for 0.6 percent of this total. Source test results indicate that about 75 percent of the POM emissions measured were in gaseous form and 25 percent were in particulate form.

[e] Approximately 95 percent of this total consists of phenanthrene (83 percent), pyrene (6 percent), and anthracene (6 percent). Benzo(a)pyrene was not detected in these emissions. Source test results indicate that about 97 percent of the POM emissions measured were in gaseous form and 3 percent were in particulate form.

[f] Approximately 96 percent of this total consists of phenanthrene (72 percent), pyrene (12 percent), fluoranthene (6 percent), and anthracene (6 percent). Benzo(a)pyrene accounts for 0.2 percent of this total. Source test results indicate that about 93 percent of the POM emissions measured were in gaseous form and 7 percent were in particulate form.

[g] Approximately 97 percent of this total consists of phenanthrene (59 percent), pyrene (17 percent), anthracene (12 percent), and fluoranthene (9 percent). Benzo(a)pyrene accounts for 0.2 percent of this total. Source test results indicate that about 98 percent of the POM emissions measured were in gaseous form and 2 percent were in particulate form.

Two references in the literature contain well-documented emission factors for individual POM species from hot mix asphalt plants. These factors are presented in Table 60, 61, and 62 to better illustrate what POMs are predominant in emissions from hot mix asphalt plants.[129,132] The results shown in Tables 60 and 61 for drum-mix plants indicate that for this type of facility, POM emissions predominantly exist in vapor form.[132] The results in Table 62 indicate that batch plant emissions are predominantly in particulate form.[129] The emission test methods used to obtain the results in Tables 60, 61, and 62 were similar with the exception of the resin type used for organics capture. An EPA Modified Method 5 sampling train was used for both plants; however, the batch-mix plant test used Tenax resin for organics collection, while the drum-mix plant test used XAD-2 resin. The effect, if any, of this difference on the POM emission results cannot be determined with the information available. However, as described in Section 5 (Source Test Procedures), XAD-2 is currently the preferred organics collection resin.

Source Locations

There are approximately 2150 companies operating an estimated 4500 hot mix asphalt plants in the United States. Approximately 40 percent of these companies operate only a single plant. Because plants must be located near the job site, plants are concentrated in areas where the highway and road network is concentrated.[127] Additional information on the locations of individual hot mix asphalt facilities can best be obtained by contacting the National Asphalt Pavement Association in College Park, Maryland.

CARBON BLACK MANUFACTURE

Process Description

The chemical carbon black consists of finely divided carbon produced by the thermal decomposition of hydrocarbons. Carbon black is a major industrial chemical used primarily as a reinforcing agent in rubber compounds, especially tires.[133] The manufacture of carbon black is of

TABLE 60. INDIVIDUAL POM SPECIES EMISSION FACTORS FOR A DRUM-MIX HOT MIX ASPHALT PLANT USING VIRGIN FEED MATERIAL[132]

POM Species	Emission Factors Under Different Control Situations: Knockout Box Control Device Only (mg POM/Mg Asphalt Produced)	Knockout Box Followed by Venturi Scrubber (mg POM/Mg Asphalt Produced)
Benz(a)anthracene	0.13	0.02
Chrysene	0.73	0.13
Benzo(b)fluoranthene	0.06	0.06
Benzo(j)fluoranthene	None detected	None detected
Benzo(e)pyrene	0.34	0.02
Benzo(a)pyrene	0.13	None detected
Indeno(1,2,3-c,d)pyrene	0.16	0.01
Phenanthrene	13.5	11.2
Anthracene	2.0	0.79
Fluoranthene	1.3	0.31
Pyrene	3.5	0.84
Benzo(k)fluoranthene	0.06	0.06
Perylene	0.06	0.02
Benzo(g,h,i)perylene	None detected	None detected
TOTAL POM[a]	22.1[b]	13.5[c]

[a] Totals may not equal sum of individual values due to rounding.

[b] Seventy-four percent of the total POM quantity was collected in the back half of the Modified Method 5 sampling system indicating that the majority of the process's POM emissions are in vapor form.

[c] Ninety-seven percent of the total POM quantity was collected in the back half of the Modified Method 5 sampling system indicating that practically all of the emissions exiting the scrubber are in vapor form.

TABLE 61. INDIVIDUAL POM SPECIES EMISSION FACTORS FOR A DRUM-MIX HOT MIX ASPHALT PLANT USING RECYCLED FEED MATERIAL[132]

POM Species	Emission Factors Under Different Control Situations: Knockout Box Control Device Only (mg POM/Mg Asphalt Produced)	Emission Factors Under Different Control Situations: Knockout Box Followed by Venturi Scrubber (mg POM/Mg Asphalt Produced)
Benz(a)anthracene	0.21	0.09
Chrysene	1.0	0.29
Benzo(b)fluoranthene	0.01	0.03
Benzo(j)fluoranthene	None detected	None detected
Benzo(e)pyrene	0.23	0.06
Benzo(a)pyrene	0.06	0.03
Indeno(1,2,3-c,d)pyrene	0.02	0.03
Phenanthrene	25.9	10.0
Anthracene	1.9	2.0
Fluoranthene	2.3	1.5
Pyrene	4.2	2.9
Benzo(k)fluoranthene	0.1	0.03
Perylene	0.04	0.02
Benzo(g,h,i)perylene	None detected	None detected
TOTAL POM[a]	35.9[b]	16.9[c]

[a] Totals may not equal sum of individual values due to rounding.

[b] Ninety-three percent of the total POM quantity was collected in the back half of the Modified Method 5 sampling system indicating that the majority of the process's POM emissions are in vapor form.

[c] Ninety-eight percent of the total POM quantity was collected in the back half of the Modified Method 5 sampling system indicating that practically all of the emissions exiting the scrubber are in vapor form.

TABLE 62. INDIVIDUAL POM SPECIES EMISSION FACTORS FOR A BATCH-MIX HOT MIX ASPHALT PLANT USING VIRGIN FEED MATERIAL[129]

POM Species	POM Emission Factor (mg/Mg Asphalt Production)[a]
Dibenzothiophene	3.6
Anthracene/phenanthrene	4.0
Methylanthracenes/phenanthrenes	6.9
9-Methylanthracene	0.4
Fluoranthene	0.7
Pyrene	0.8
Benzo(c)phenanthrene	0.3
Chrysene/benz(a)anthracene	0.5
7,12-Dimethylbenz(a)anthracene	0.3
3,4-Benzofluoranthene	0.4
Benzo(a)pyrene/benzo(e)pyrene/perylene	0.3
3-Methylcholanthrene	0.3
Dibenz(a,h)anthracene	0.3
Indeno(1,2,3-c,d)pyrene	0.3
7H-Dibenzo(c,g)carbazole	0.3
Dibenzo(a,h and a,i)pyrene	0.3
TOTAL POM	19.7[b]

[a] These emission factors apply to the final stack (scrubber stack) emissions of a batch hot mix asphalt plant. The POM emissions have originated in the rotary dryer and mixer operations of the process. Emissions were vented to a cyclone and then to a wet scrubber.

[b] An average of 90 percent of the POMs were collected in the front half of the Modified Method 5 sampling train indicating that emissions were primarily in particulate form.

potential concern for POM emissions because the predominantly used production process involves the combustion of natural gas and the high-temperature pyrolysis of aromatic liquid hydrocarbons.

Approximately 90 percent of all carbon black produced in the United States is manufactured by the oil-furnace process, a schematic of which is given in Figure 28.[133,134] The process streams identified in Figure 28 are defined in Table 63. Generally, all oil-furnace carbon black plants are similar in overall structure and operation. The most pronounced differences in plants are primarily associated with the details of decomposition furnace design and raw product processing.[133] Other processes used for carbon black production are thermal decomposition of natural gas and exothermic decomposition of acetylene.[134]

In the oil-furnace process, carbon black is produced by the pyrolysis of an atomized liquid hydrocarbon feedstock in a refractory-lined steel furnace. Processing temperatures in the steel furnace range from 1320 to 1540°C (2408 to 2804°F). The heat needed to accomplish the desired hydrocarbon decomposition reaction is supplied by the combustion of natural gas.[133,135]

Feed materials used in the oil-furnace process consist of petroleum oil, natural gas, and air. Also, small quantities of alkali metal salts may be added to the oil feed to control the degree of structure of the carbon black.[134] The ideal raw material for the production of modern, high structure carbon blacks is an oil which is highly aromatic, low in sulfur, asphaltenes and high molecular weight resins, and substantially free of suspended ash, carbon, and water. The reactor for the oil furnace process consists of a refractory-lined steel furnace which is from 1.5 to 9 m (4.9 to 29.5 ft) in length and 0.15 to 0.76 m (0.49 to 2.5 ft) in internal diameter. To provide maximum efficiency, the furnace and burner are designed to separate, insofar as possible, the heat generating reaction from the carbon forming reaction. Thus, the natural gas feed (stream 2 in Figure 28) is burned to completion with preheated air (stream 3) to produce

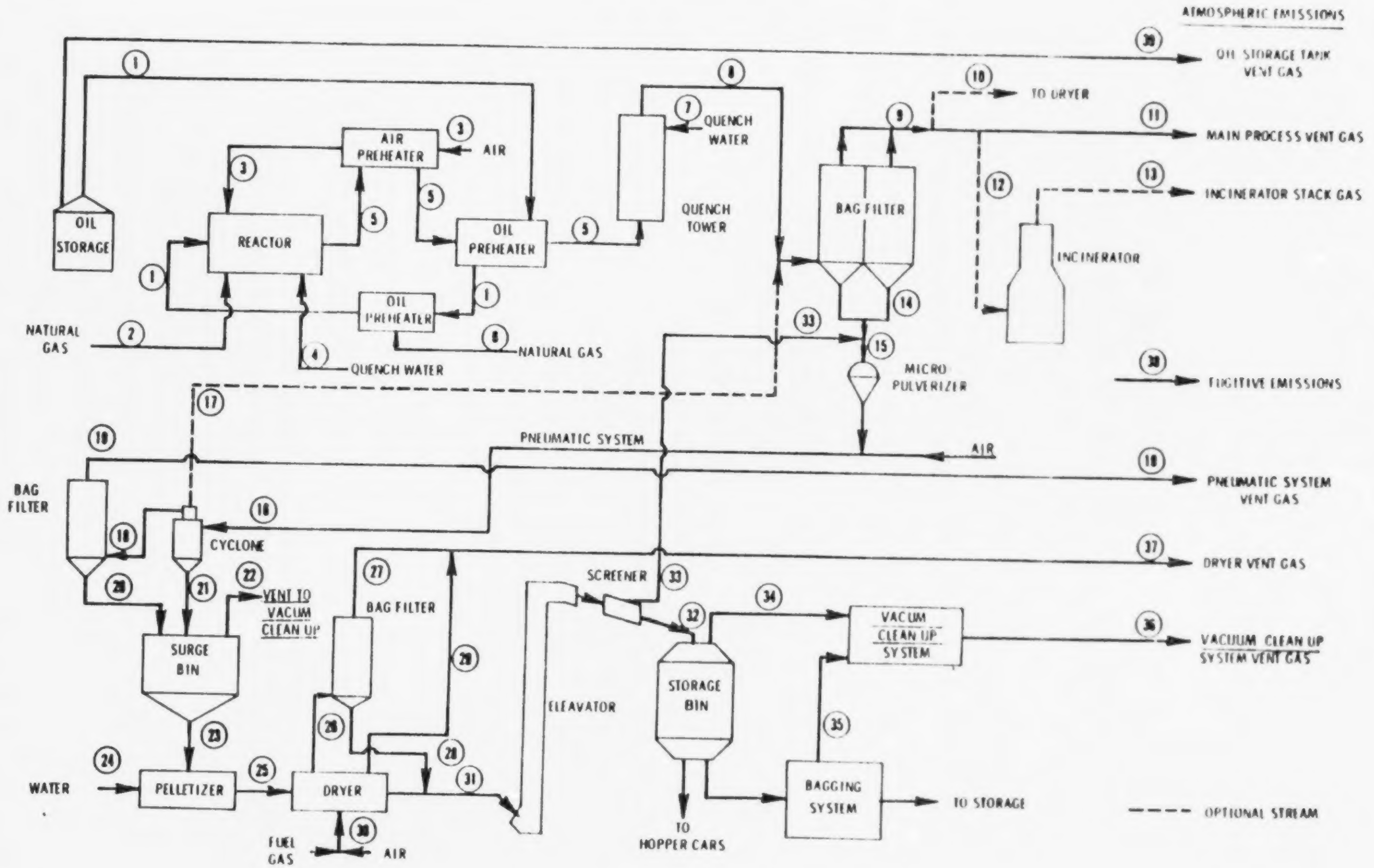

ATMOSPHERIC EMISSIONS
OIL STORAGE
NATURAL GAS
REACTOR
AIR PREHEATER
AIR
OIL PREHEATER
OIL PREHEATER
NATURAL GAS
QUENCH WATER
QUENCH WATER
QUENCH TOWER
BAG FILTER
MICRO PULVERIZER
AIR
TO DRYER
INCINERATOR
OIL STORAGE TANK VENT GAS
MAIN PROCESS VENT GAS
INCINERATOR STACK GAS
FUGITIVE EMISSIONS
PNEUMATIC SYSTEM
PNEUMATIC SYSTEM VENT GAS
DRYER VENT GAS
VACUUM CLEAN UP SYSTEM VENT GAS
BAG FILTER
CYCLONE
VENT TO VACUM CLEAN UP
SURGE BIN
WATER
PELLETIZER
DRYER
FUEL GAS
AIR
BAG FILTER
ELEAVATOR
SCREENER
STORAGE BIN
TO HOPPER CARS
VACUM CLEAN UP SYSTEM
BAGGING SYSTEM
TO STORAGE
OPTIONAL STREAM
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39

Figure 28. Process flowsheet for an oil-furnace carbon black plant.[134]

TABLE 63. STREAM CODE FOR THE OIL-FURNACE PROCESS ILLUSTRATED IN FIGURE 28[133]

Stream	Identification
1	Oil feed
2	Natural gas feed
3	Air to reactor
4	Quench water
5	Reactor effluent
6	Gas to oil preheater
7	Water to quench tower
8	Quench tower effluent
9	Bag filter effluent
10	Vent gas purge for dryer fuel
11	Main process vent gas
12	Vent gas to incinerator
13	Incinerator stack gas
14	Recovered carbon black
15	Carbon black to micropulverizer
16	Pneumatic conveyor system
17	Cyclone vent gas recycle
18	Cyclone vent gas
19	Pneumatic system vent gas
20	Carbon black from bag filter
21	Carbon black from cyclone
22	Surge bin vent
23	Carbon black to pelletizer
24	Water to pelletizer
25	Pelletizer effluent
26	Dryer direct heat source vent
27	Dryer bag filter vent
28	Carbon black from dryer bag filter

TABLE 63. STREAM CODE FOR THE OIL-FURNACE PROCESS ILLUSTRATED IN FIGURE 28[133] (Continued)

Stream	Identification
29	Dryer indirect heat source vent
30	Hot gases to dryer
31	Dried carbon black
32	Screened carbon black
33	Carbon black recycle
34	Storage bin vent gas
35	Bagging system vent gas
36	Vacuum cleanup system vent gas
37	Dryer vent gas
38	Fugitive emissions
39	Oil storage tank vent gas

a temperature of 1320 to 1540°C (2408 to 2804°F). The reactor is designed so that this zone of complete combustion attains a swirling motion, and the oil feed (stream 1), preheated to 200 to 370°C (392 to 698°F), is sprayed into the center of the zone. Preheating is accomplished by heat exchange with the reactor effluent and/or by means of a gas-fired heater. The oil is cracked to carbon and hydrogen with side reactions producing carbon oxides, water, methane, acetylene and other hydrocarbon products. The heat transfer from the hot combustion gases to the atomized oil is enhanced by highly turbulent flow in the reactor.[134]

The reactor converts 35 to 65 percent of the feedstock carbon content to carbon black, depending on the feed composition and the grade of black being produced. The yields are lower for the smaller particle size grades of black. Variables that can be adjusted to produce a given grade of black include operating temperature, fuel concentration, space velocity in the reaction zone, and reactor geometry (which influences the degree of turbulence in the reactor). A typical set of reactor operating conditions is given below for high abrasion furnace carbon black.[134]

Parameter	Value
Rate of oil feed	0.76 m^3/hr
Preheat temperature of oil	288°C
Rate of air feed	6653 m^3/hr
Rate of natural gas feed	623 m^3/hr
Furnace temperature in reaction zone	1400°C
Rate of carbon black production	390 kg/hr
Yield of black (based on carbon in oil feed)	60 percent

The hot combustion gases and suspended carbon black are cooled to about 540°C (1004°F) by a direct water spray in the quench area, which is located near the reactor outlet. The reactor effluent (stream 5 in Figure 28) is further cooled by heat exchange in the air and oil preheaters. It is then sent to a quench tower where direct water sprays finally reduce the stream temperature to 230°C (446°F).

Carbon black is recovered from the reactor effluent stream by means of a bag filter unit. The carbon black laden gases from the quench tower (stream 8 in Figure 28) enter the bag filter hopper trough below the bag cell plates at 200 to 230°C (392 to 446°F). The gases flow into the individual bags of each compartment through the cell plates. The carbon black collects on the inside of the bags and the filtered gas flows through the bags and out the bag filter stacks. During the cleaning cycle of each compartment, the black is removed from the bag fabric and drops back into the hopper trough. It passes from the hopper through a hammer mill that breaks up the lumps and is then transported to the product treatment section of the plant via a pneumatic conveyor system (stream 16).[134]

The exhaust gas from the bag filter unit (stream 9 in Figure 28) is vented directly to the atmosphere in most carbon black plants. Alternatively, it may be sent to a flare or incinerator to reduce the contaminant loading (stream 12). In addition, 13 to 15 percent of the effluent (stream 10) may be diverted to produce auxiliary fuel for the raw product drying operation.

The raw carbon black collected in the bag filter unit must be further processed to become a marketable product. After passing through the pulverizer, the black has a bulk density of 24 to 59 kg/m^3, and it is too fluffy and dusty to be transported. It is therefore converted into pellets or beads with a bulk density of 97 to 171 kg/m^3. In this form, it is dust-free and sufficiently compacted for shipment.

The carbon black is collected from the pneumatic system (stream 16) by means of a cyclone, a bag filter, or a cyclone and bag filter in combination. When a cyclone is used, the exhaust gas (stream 17) is recycled to the primary bag filter unit. When a bag filter is used, the exhaust gas (stream 19) is vented to the atmosphere. The recovered carbon black is collected in a covered surge bin. The carbon black is fed from the surge bin via a screw conveyor to the pelletizer, where it is mixed with one part of water to two parts of black. A binding agent such as molasses, sugar, dextrin, or starch, may be added to the pelletizing water. The pelletizer is a horizontal housing that contains a revolving axial shaft with pins or spikes mounted on its periphery. Agitation by the pins causes the mixture of carbon black and water to form nearly spherical particles 1.6 to 3.2 mm (0.06 to 0.13 in) in diameter. The pellets are then conveyed to a dryer for removal of the water.[134]

Rotating horizontal drums operating at 190 to 230°C (374 to 392°F) are typically used for product drying in carbon black processes. The dryers are fueled by natural gas, which may be augmented by a portion of the main process vent gas. From 35 to 70 percent of the combustion gas is charged directly to the interior of the dryer. After passing through the dryer, this stream (stream 26) is sent to a bag filter for removal of entrained carbon black before being vented to the atmosphere. The remaining 30 to 65 percent of the combustion gas (stream 29) acts as an indirect heat source for the dryer and is vented directly to the atmosphere.

The dried, pelletized carbon black (stream 31) is screened and sent to a covered storage bin via a bucket elevator. Oversize pellets are removed in the screener and recycled (stream 33) to the pulverizer. From the product storage bin, the carbon black can be loaded into railroad hopper cars for bulk shipment or sent to a vacuum bagging system which is hermetically sealed to prevent emission of carbon black.[134]

Exhaust gas from the bag filter unit constitutes the main process vent and the largest source of POM emissions. About two-thirds of the United States carbon black plants treat the bag filter exhaust stream to control carbon monoxide and hydrocarbon emissions. Combustion in thermal incinerators, flares, or carbon monoxide boilers is used for treating the gases. In the remaining facilities, bag filter exhaust emissions are vented directly to the atmosphere.[135] Emissions from product dryers are predominantly controlled by high efficiency bag filter units; however, water scrubbers are also used at a few facilities.[134]

Polycyclic organic matter emissions associated with raw carbon black production (exclusive of additional processing steps) appear to be a function of the efficiency of the product recovery bag filter and, where applicable, the destructive or potentially constructive effect of hydrocarbon and carbon monoxide combustion control devices. Because decreased efficiency in the product recovery bag filter unit means decreased carbon black production and lost revenues, it is likely that these bag filters are maintained by companies at optimum conditions. The use of combustion control devices in a majority of plants would be expected to reduce POM emissions by destructing them into constituent compounds and elements (water, carbon dioxide, nitrogen); however, some investigators have speculated that POM compounds are being formed in the high temperature zone of the hydrocarbon and carbon monoxide control devices.[133] No data were supplied in Reference 133 to support this POM formation theory.

Emission Factors

Several emission factors for POM emissions from carbon black manufacturing were identified in the literature. All identified emission factors are applicable to emissions from the main process vent. No emissions data of any type were available for potential POM sources associated with raw product processing such as grinding, drying, and packaging.

The best documented emission factor for POM emissions from carbon black manufacturing is that developed by Serth and Hughes in Reference 133. Total uncontrolled POM emissions from the main process vent (product recovery baghouse) were measured in a series of three tests with the average emission factor being 1900 mg/Mg (0.0039 lb/ton) of carbon black produced. Of the total 1900 mg, 42 percent were acenaphthylene, 26 percent pyrene, and 12 percent methyl- and dimethylanthracenes/phenanthrenes. Known carcinogenic species constituted about 8 percent by weight of the total POM quantity.[133] A breakdown of all POM compounds that were identified is given in Table 64.[133]

TABLE 64. INDIVIDUAL POM COMPOUNDS MEASURED IN THE TEST OF AN OIL-FURNACE CARBON BLACK PLANT[133]

POM Compound	Mean Emission Factor, mg/Mg (lb/ton)[a,b,c,d]
Acenaphthylene	800 (0.002)
Anthracene/phenanthrene	70 (0.0001)
Benzo(c)phenanthrene	<2 (trace)
Benzofluoranthenes	30 (0.00006)
Benzo(g,h,i)fluoranthene	40 (0.00008)
Benzo(g,h,i)perylene/anthanthrene	23 (0.00005)
Benzopyrenes and perylene	30 (0.00006)
Chrysene/benz(a)anthracene	9 (0.00002)
Dibenzanthracenes	<2 (trace)
Dibenzo(c,g)carbazole	<2 (trace)
Dibenzopyrenes	<2 (trace)
Dibenzothiophene	14 (0.00003)
Dimethylanthracenes/phenanthrenes	140 (0.0003)
7,12-Dimethylbenz(a)anthracene	70 (0.0001)
Fluoranthene	60 (0.0001)
Indeno(1,2,3-c,d)pyrene	<2 (trace)
Methylanthracenes/phenanthrenes	100 (0.0002)
Methylcholanthrene	<2 (trace)
Methylfluoranthene/pyrene	23 (0.00005)
Pyrene	500 (0.001)
TOTAL	1900 (0.0039)

[a] Units are in terms of mg POM/Mg of carbon black produced.

[b] Values given are the average of three test runs.

[c] Values are for uncontrolled emissions from the product recovery baghouse of an oil-furnace carbon black plant.

[d] Emission factors represent particulate and gaseous POM compound constituents.

All POM sampling in the Serth and Hughes work was conducted using a EPA Modified Method 5. A gas cooler and organics trap containing XAD-2 resin were used to recovery vaporous POM that may be released from the process vent. All POM samples were separated using liquid chromatography and analyzed using gas chromatography-mass spectrometry.[133]

A second set of POM emission factor data for carbon black plants was identified that gave total POM emission factors ranging from 220 mg/Mg (0.00045 lb/ton) of carbon black produced to 490 mg/Mg (0.001 lb/ton), with the average being 340 mg/Mg (0.0007 lb/ton).[136] These data were not as well documented as Reference 133 data in that it was not specified exactly what emission point the factor applied to and if it was for controlled or uncontrolled emissions. Of the range of values determined, the 490 mg/Mg value was deemed by Reference 136 to be the most reliable because it was measured using a Method 5 train followed by a Tenax adsorbent sampler. All samples were analyzed by gas chromatography-mass spectrometry.[136]

In a single test measurement by Battelle of main process vent emissions from an oil-furnace carbon black plant, an uncontrolled total POM emission factor of 91 mg/Mg (0.0002 lb/ton) was determined. No information is available to define the individual POM species measured or the techniques used to sample and analyze for POM.[134,137]

A summary of available POM emission factors for carbon black production by the oil-furnace process is given in Table 65.

Source Locations

In 1985, there were 27 carbon black manufacturing facilities in the continental United States and one facility in Puerto Rico. Almost 75 percent of all carbon black production occurs in the States of Texas and Louisiana (41 and 33 percent, respectively). The location of all facilities and their estimated annual production capacities in 1985 are provided in Table 66.[138]

TABLE 65. SUMMARY OF POM EMISSION FACTORS FOR OIL-FURNACE CARBON BLACK PLANTS

Data Sources	Total POM Emission Factor, mg/Mg (lb/ton)[a]
References 133 and 134 (Monsanto data)	1200 - 3000 (0.0024 - 0.0061) Avg. 1900 (0.0039)[b,c]
Reference 136 (EEA data)	220 - 490 (0.00045 - 0.001) Avg. 340 (0.0007)[d]
References 134 and 137 (Battelle data)	91 (0.0002)[e]

---

[a] Factors are in terms of mg POM emissions per Mg of carbon black produced.

[b] Factors are for uncontrolled emissions from the main process vent.

[c] Forty-two percent of the emissions is acenaphtylene, 26 percent is pyrene, and 12 percent is methyl- and dimethylanthracenes/phenanthrenes.

[d] Factors are for uncontrolled emissions. It is assumed that emissions were measured from the main process vent. Particulate and gaseous POM components are represented.

[e] Factors are for uncontrolled emissions from the main process vent. Anthracene, phenanthrene, fluoranthene, pyrene, benzo(a)pyrene, benz(a)-anthracene, and chrysene were identified as constituents of total POM. Anthracene/phenanthrene constituted 63 percent of total POM, pyrene 28 percent, and fluoranthene 7 percent. Benzo(a)pyrene made up only 0.09 percent of total POM.

TABLE 66. LOCATIONS AND ANNUAL CAPACITIES OF CARBON BLACK PRODUCERS IN 1985[138]

Company	Facility Location	Annual Capacity, Gg (10^6 lbs)[a]
Ashland Oil, Inc.	Aransas Pass, TX	75 (165)
	Belpre, OH	54 (120)
	New Iberia, LA	127 (280)
Cabot Corporation	Franklin, LA	104 (230)
	Pampa, TX	27 (60)
	Villa Platte, LA	122 (270)
	Waverly, WV	73 (160)
Chevron Corporation	Cedar Bayou, TX[b]	9 (20)
	Conroe, TX	52 (115)
	El Dorado, AR	49 (108)
	Mojave, CA	24 (54)
	Moundsville, WV	73 (162)
	North Bend, LA	110 (242)
	Ulysses, KS	38 (84)
Ebonex Corporation	Melvindale, MI[c]	5 (10)
General Carbon Company	Los Angeles, CA[c]	<0.5 (<1)
Hoover Color Corporation	Irvington, NJ[c]	<0.5 (<1)
J. M. Huber Corporation	Baytown, TX	100 (220)
	Borger, TX	91 (200)
Mobay Chemical Corporation	Hawthorne, NJ[d]	<0.5 (<1)
Phillips Petroleum Company	Borger, TX	125 (275)
	Orange, TX	61 (135)
Sid Richardson Carbon and Gasoline Company	Addis, LA	61 (120)
	Big Spring, TX	50 (110)
Union Carbide Corporation	Penuelas, PR[b]	4 (8)

TABLE 66. LOCATIONS AND ANNUAL CAPACITIES OF CARBON BLACK PRODUCERS IN 1985[138] (Continued)

Company	Facility Location	Annual Capacity, Gg (10^6 lbs)[a]
Witco Chemical Corporation	Phenix, City, AL	25 (55)
	Ponca City, OK	57 (125)
	Sunray, TX	45 (100)
TOTAL		1556 (<3431)

[a] Capacities as of January 1, 1985.

[b] Facility does not use the oil-furnace method of carbon black production, acetylene decomposition is used instead to produce acetylene black.

[c] Facility uses incomplete combustion of natural gas and not the oil-furnace method to produce carbon black.

[d] Carbon black is produced at this facility only for pigment uses.

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility if a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

SECONDARY LEAD SMELTING

Process Description

One source test of a secondary lead smelting facility has indicated that secondary lead smelters processing batteries and battery scrap to recover lead are potential sources of POM emissions.[139] The source of POM emissions has been theorized to be the polymeric organic casings (plastic and rubber) on batteries, which upon combustion in high temperature smelting furnaces form POM compounds.[139,140]

The secondary lead smelting industry produces lead and lead alloys by reclaiming lead from scrap. Secondary lead may be refined to produce soft lead (pure) or alloyed to produce a variety of hard lead alloys. Most of the lead produced by secondary lead smelters is hard lead used in the production of lead-acid batteries. Scrap automobile batteries are the largest single source of lead-bearing raw material. These batteries contain approximately 8.2 kg (18 lbs) of lead per battery consisting of 40 percent lead alloys and 60 percent lead oxide.

Sources of lead-bearing metal used by secondary lead smelters include scrap batteries from junk dealers, battery plant scrap, and other miscellaneous scrap. Certain facilities, however, rely exclusively on non-battery scrap such as wheel balance weights, pipe, solder, drosses, and lead-sheathed cable.[141]

As illustrated in Figure 29, the normal sequence of operations in a secondary lead smelter are scrap receiving, charge preparation, furnace smelting, and lead refining and alloying. In the majority of plants, scrap batteries are first sawed or broken open to remove the lead alloy plates and lead oxide paste material. The removal of battery covers is typically accomplished using an automatic battery feed conveyor system and a slow speed saw. Hammer mills or other crushing/shredding devices are utilized to break open battery cases once covers are removed. Float/sink separation

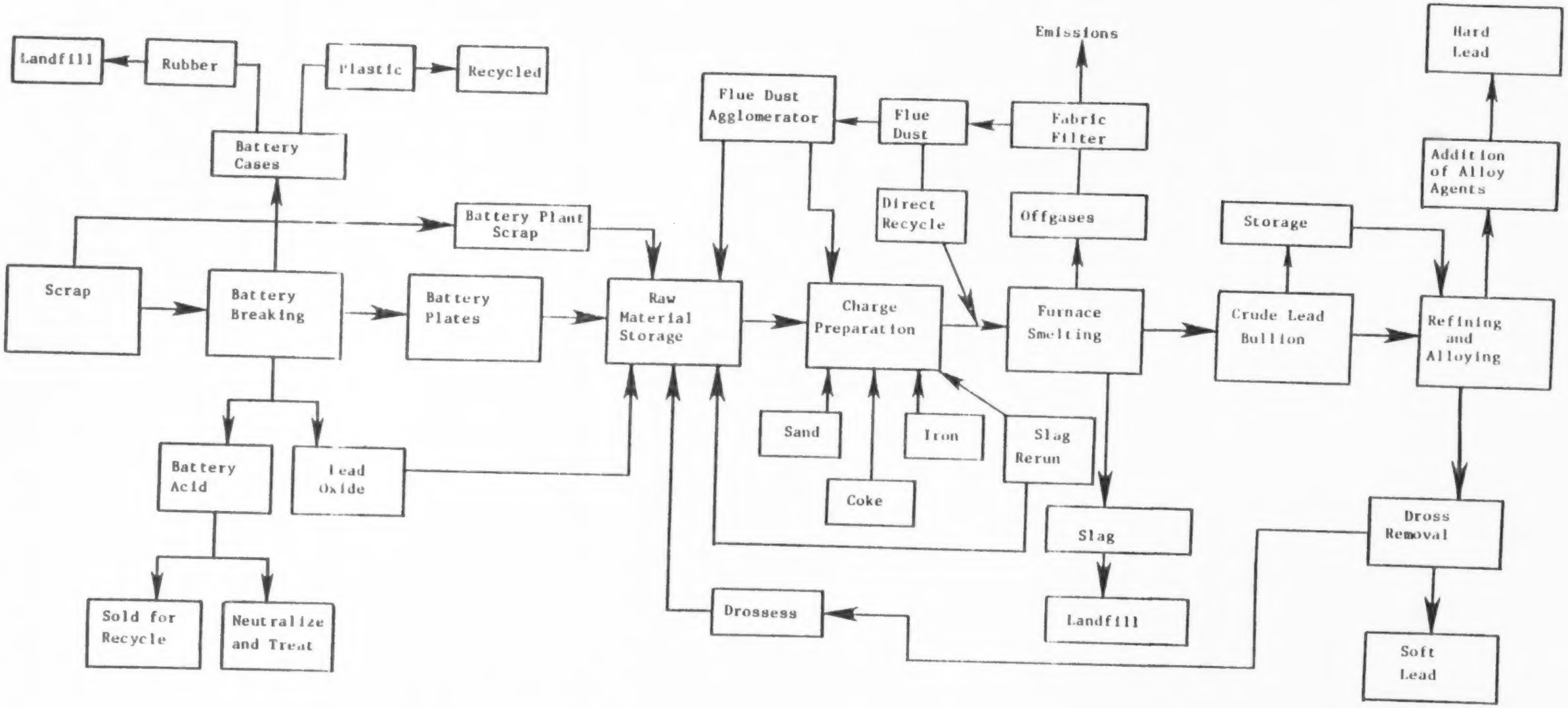

Landfill
Rubber
Plastic
Recycled
Battery Cases
Scrap
Battery Breaking
Battery Plant Scrap
Battery Plates
Battery Acid
Lead Oxide
Sold for Recycle
Neutralize and Treat
Raw Material Storage
Drossess
Flue Dust Agglomerator
Flue Dust
Direct Recycle
Charge Preparation
Sand
Coke
Iron
Slag Rerun
Emissions
Fabric Filter
Offgases
Furnace Smelting
Slag
Landfill
Storage
Crude Lead Bullion
Hard Lead
Addition of Alloy Agents
Refining and Alloying
Dross Removal
Soft Lead

Figure 29. Sequence of operations at a typical secondary lead smelter.[141]

systems are typically used to separate plastic battery parts, lead terminals, lead oxide paste, and rubber parts. The majority of lead smelters recover the crushed plastic materials for recycling. Rubber casings are usually landfilled. In smelters where battery covers and casings are removed prior to charging the lead contents into smelting furnaces, the potential for POM formation should be greatly reduced. Plants charging whole batteries to smelting furnaces (a minority of plants) without any preparation to remove covers and casings would present the greatest potential for POM emissions from the smelting furnace.

After removing the lead components from the charge batteries, the lead scrap is combined with other charge materials such as refining drosses, flue dust, furnace slag, coke, limestone, sand, and scrap ion and fed to either a blast, reverberatory, or rotary smelting furnace. Smelting furnaces are used to produce crude lead bullion which is refined and/or alloyed into final lead products. Of the 35 existing secondary lead smelters, 17 use a blast furnace, 8 operate both a blast and reverberatory or rotary furnace, 5 operate a reverberatory furnace, and 5 use a rotary furnace.[141]

A simplified flow diagram of a single secondary lead blast furnace system is presented in Figure 30. Blast furnaces are fueled by coke to reach smelting operating temperatures of from 430-1320^{o}C (800-2400^{o}F). As the charge material melts, the iron, silica, and limestone form an oxidant-retardent flux which floats to the top of the melt. Molten lead bullion in the bottom of the furnace is tapped almost continuously and cast into large one ton blocks called buttons or sows. Blast furnaces are operated in both batch and semi-continuous modes. A typical production range for blast furnaces is 18 to 73 Mg (20 to 80 tons)/day of lead bullion.[141]

The emission stream from a blast furnace is typically controlled by knockout boxes, an afterburner, U-tube coolers, and a baghouse. Knockout boxes are used to collect large particulate matter, which separates from the gas flow in the ducts. Afterburners are used to destroy organic emissions.

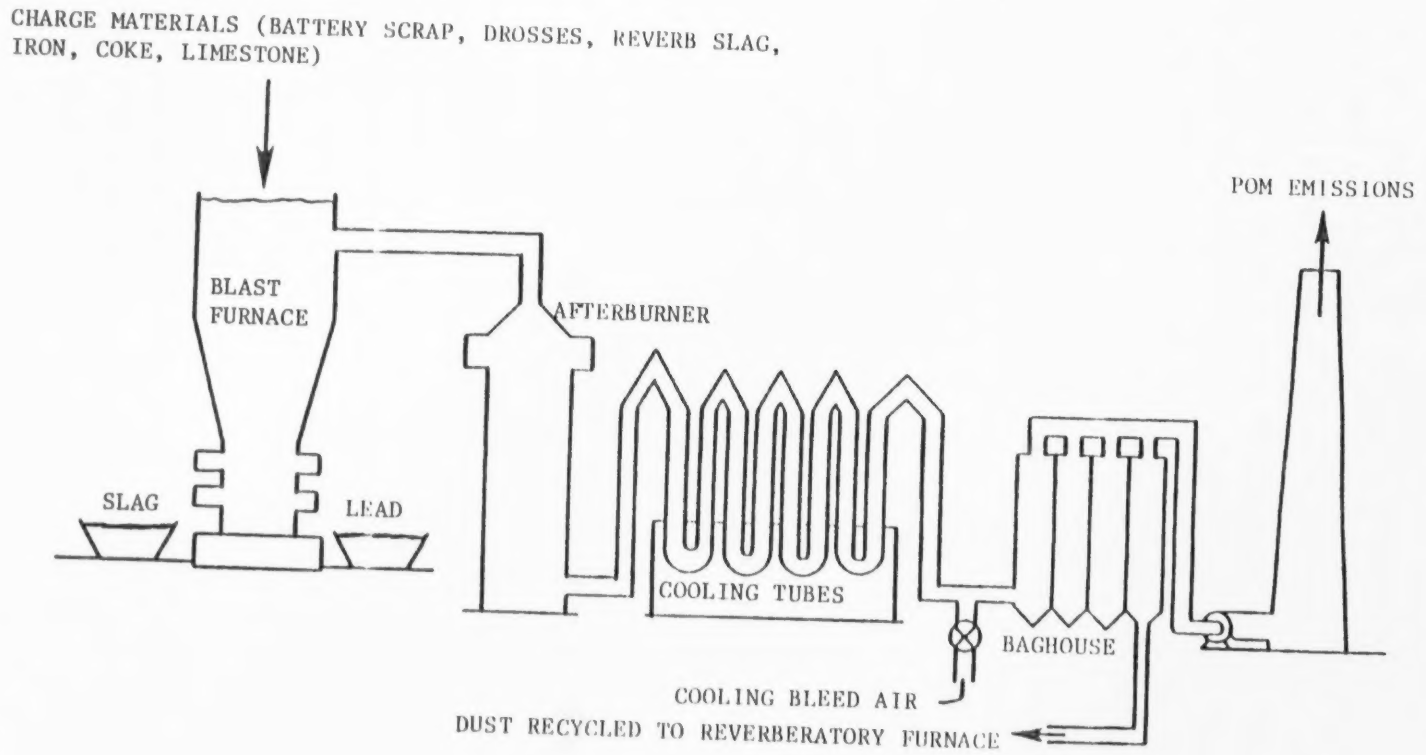

CHARGE MATERIALS (BATTERY SCRAP, DROSSES, REVERB SLAG,
IRON, COKE, LIMESTONE)
BLAST
FURNACE
SLAG
LEAD
AFTERBURNER
COOLING TUBES
BAGHOUSE
COOLING BLEED AIR
DUST RECYCLED TO REVERBERATORY FURNACE
POM EMISSIONS

Figure 30. Typical blast furnace system for secondary lead production.[141]

U-tube coolers are used to lower the temperature of the gas stream prior to its ventilation to the baghouse to reduce overall particulate matter emissions. Baghouse dusts are frequently recycled to the blast furnace.

Smelters using reverberatory furnaces typically have configurations similar to that shown in Figure 31.[141] Reverberatory furnaces are fired with either gas or oil. Charge materials are heated by radiation from the burner flames and from the furnace walls. As indicated in Figure 31, reverberatory furnace charge material typically includes lead scrap, battery plates, lead oxides, and recycled flue dusts. Fresh charge material is added to the furnace as more of the solid material in the furnace becomes liquid. Material melting in reverberatory furnace takes place at temperatures of about 1260°C (2300°F) and near atmospheric pressure.[141] Molten, semi-soft lead is periodically tapped from the furnace and placed into molds. Reverberatory furnaces generally produce lead that is purer than that obtained from blast furnaces. A typical reverberatory furnace produces about 45 Mg (50 tons)/day of lead product. Of the total amount of material input to a reverberatory furnace process, approximately 47 percent is recovered as lead, 46 percent is slag, and 7 percent leaves the furnace as particulate and metal fume.[141]

Rotary furnaces in the secondary lead industry, which are very similar in operation to reverberatory furnaces, are much less common in the United States than in industrialized European nations. The rotary furnace is a batch feed unit that rotates slowly during the heating of the charge material. One major difference between the rotary furnace and the reverberatory furnace is that about 70 percent of the sulfur contained in the rotary furnace charge material is removed in the slag. This is accomplished by using relatively large amounts of iron (in the form of cast iron borings) in the rotary furnace feed. Iron serves the following distinct purposes.

- it promotes the reduction of lead sulfate and lead oxide to metallic lead

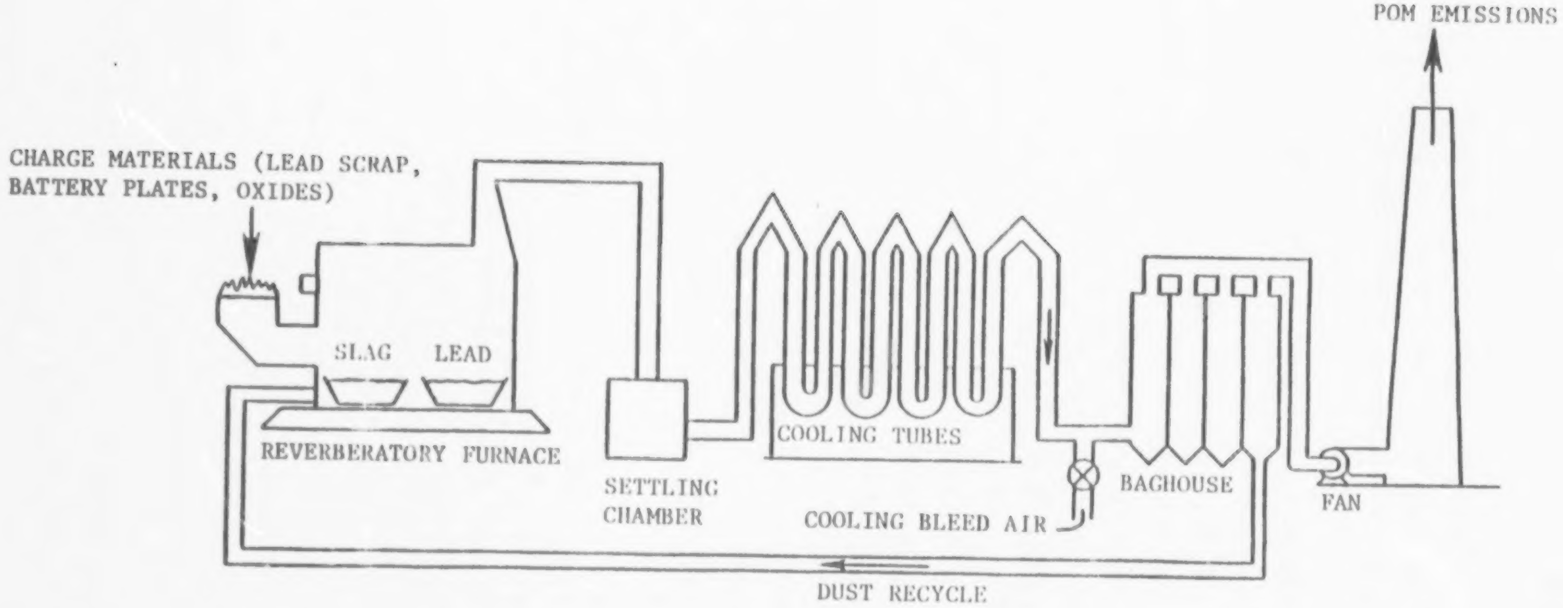

POM EMISSIONS
CHARGE MATERIALS (LEAD SCRAP, BATTERY PLATES, OXIDES)
SLAG
LEAD
REVERBERATORY FURNACE
SETTLING CHAMBER
COOLING TUBES
COOLING BLEED AIR
BAGHOUSE
FAN
DUST RECYCLE

Figure 31. Typical reverberatory furnace system for secondary lead production.[141]

- it complexes with most of the available sulfur and removes it in the slag

Consequently, sulfur dioxide concentrations in rotary furnace exhausts are much lower than those at smelters using blast or reverberatory furnaces.[141]

Rotary furnace charge materials typically consist of lead paste, batteries, cast iron borings, anthracite, limestone, and soda ash. Natural gas or fuel oil is used to heat these furnaces to smelting temperatures of 1260 to 1320°C (2300 to 2400°F). Semi-soft lead product is periodically tapped from rotary furnaces and put into molds to await further refining processes.

Reverberatory and rotary furnaces typically use an emissions control design consisting of an exhaust gas settling chamber, U-tube coolers, and a baghouse for final emissions control. Dusts collected by the baghouse are recycled to the furnace as charge material.

As shown in Figure 29, crude lead bullion produced by blast, reverberatory, or rotary furnaces undergoes refining and alloying processes to produce final lead products. Refining and alloying processes are performed in pot furnaces or refining kettles. The process is a batch operation and may take from a few hours to 2 to 3 days depending upon the degree of purity or alloy type required. Refining kettles are gas- or oil-fired and have typical capacities of 23 to 136 Mg (25 to 150 tons) of lead. Refining and alloying activities are conducted at temperatures ranging from 320 to 700°C (600 to 1300°F). When soft lead is desired as a final product, contaminant elements are removed through careful temperature control and by the addition of dross-forming agents. Soft lead refining typically produces refined metal that is greater than 99.97 percent pure lead.[141]

The production of soft lead typically involves five refining steps. In the first step, the lead is heated to approximately 370 to 510°C (700 to 950°F) which results in the formation of a light dross. This dross consists of lead oxides and other impurities and appears as a dusty black powder. After removing the light dross, the temperature of the lead is reduced to 300 to 370°C (575 to 700°F) in preparation for the second step, which involves the addition of sulfur for the removal of copper. After removing the copper drosses, the kettle temperature is increased to 510 to 650°C (950 to 1200°F) in preparation for the third step. Sodium nitrate is used as a drossing agent for the purpose of removing tin. The yellow tin drosses are stored and used as special charge material for the production of high tin content blast furnace metal. The fourth step takes place at 540 to 700°C (1000 to 1300°F) and involves the addition of sodium nitrate for the removal of antimony and arsenic drosses. The last step is a final cleaning carried out by the addition of sulfur or caustic soda at a lower temperature.[141]

Hard lead alloys may be classified as either antimonial or non-antimonial lead alloys. The major alloying agents required in antimonial lead are antimony, arsenic, and tin. The production of antimonial lead alloys generally requires the addition of these elements and the removal of copper. Alloying agents are generally added at a kettle temperature of 425 to 480°C (800 to 900°F). The major alloying agent used in non-antimonial lead alloys is calcium. To produce calcium-lead alloys, antimony, arsenic, and tin must first be removed by refining. These elements, which act as hardening agents in other alloys, are replaced by copper, sulfur, and selenium.

Following the final refining step, a sample of the refined metal is collected, and the alloying specifications are verified by chemical analysis. When the desired composition is reached, the molten metal is pumped from the kettle into the casting machine and cast into lead ingots which are rectangular bars weighing approximately 25 kg (56 lbs) each.[141]

Emission Factors

One set of data have been identified that quantify POM emissions from a secondary lead smelter processing batteries. Four emission samples have been obtained from one facility. The data measured were POM concentrations

TABLE 67. POM CONCENTRATIONS IN STACK GASES OF A SECONDARY LEAD SMELTER[140]

POM Compound[a]	Compound Concentrations (ng/Nm^3)[b,c,d]			
	Sample 1	Sample 2	Sample 3	Sample 4
Anthracene/phenanthrene	600	740	770	940
Methyl anthracenes	25	34	41	33
Fluoranthene	160	170	330	310
Pyrene	31	22	28	30
Methyl pyrenes/fluoranthenes	2	2	3	2
Benzo(c)phenanthrene	10	11	17	13
Chrysene/benz(a)anthracene	25	23	28	25
Benzo(a)pyrene	1	1	1	1

[a] This list of POM compounds represents all that were identified in the stack gases and not a restricted list of just certain compounds that were analyzed for.

[b] Sampling and analysis procedures were designed to measure particulate and vaporous POM.

[c] Concentrations represent controlled emissions because measurements were taken in the exhaust stack after the final control device. The type of control device used was not specified.

[d] Samples 1 and 2 were taken during one visit to the smelter and samples 3 and 4 were taken during a later visit to the same smelter.

in the stack gases following the final control device. These concentrations are given in Table 67.[140] The predominant POM compounds measured were anthracene/phenanthrene and fluoranthene. Benzo(a)pyrene was measured but its levels were only 0.1 percent of the anthracene/phenanthrene levels. The sampling and analysis procedures used during the tests of the secondary lead smelter contained mechanisms to capture and measure both particulate and vaporous POM.[140] The majority of the POM measured was caught in the sampling train's water impingers.[140]

The consistency of the POM data across all samples is atypical for POM emission sources. Both the results for samples taken on the same day and the total results for all samples demonstrate a reproducibility that is unexpected. The relative magnitudes of each POM compound measured are consistent from sample 1 to sample 4.

Source Locations

As of May 1985, the secondary lead smelting industry consisted of 43 facilities operated by 27 companies. A list of the 43 facilities and their locations is given in Table 68.[141]

PRIMARY ALUMINUM PRODUCTION

Process Description

All primary aluminum in the United States is produced by the electrolytic reduction of alumina otherwise known as the Hall-Heroult process.[142] The general procedures for primary aluminum reduction are illustrated in Figure 32.[142] Aluminum reduction is carried out in shallow rectangular cells (pots) made of carbon-lined steel with carbon blocks that are suspended above and extend down into the pot (Figure 33). The pots and carbon blocks serve as cathodes and anodes, respectively, for the electrolytical process.[142-144]

TABLE 68. SECONDARY LEAD SMELTERS IN THE UNITED STATES IN 1985[141]

State	City	Company
Alabama	Leeds	Interstate Lead Company, Inc.
	Troy	Sanders Lead Company
California	Anaheim	Delco Remy
	City of Industry	Quemetco/RSR Corporation
	Gardena	Alco Pacific
	San Francisco	Federated Metals/ASARCO
	Vernon	GNB Batteries/Gould, Inc.
Florida	Tampa	Chloride Metals
	Tampa	Gulf Coast Lead
Georgia	Atlanta	National Smelting
	Atlanta	Seitzinger/Taracorp
	Columbus	Chloride Metals
	Fitzgerald	Delco Remy
Illinois	Chicago	Inland Metals
	Granite City	Taracorp
Indiana	Beech Grove	Refined Metals
	East Chicago	U. S. S. Lead
	Indianapolis	Quemetco/RSR Corporation
	Muncie	Delco Remy
Kansas	Olathe	Delco Remy
Louisiana	Baton Rouge	Schuylkill Metals
Minnesota	Eagan	Gopher Smelting
Missouri	Forest City	Schuylkill Metals
New Jersey	New Brunswick	Delco Remy
	Newark	Federated Metals/ASARCO
	Pedricktown	National Smelting
New York	East Syracuse	Roth Brothers Smelting
	Middletown	Revere Smelting and Refining Corporation of New Jersey/ RSR Corporation

TABLE 68. SECONDARY LEAD SMELTERS IN THE UNITED STATES IN 1985[141] (Continued)

State	City	Company
Ohio	Cleveland	Master Metals
Oregon	St. Helens	Bergsoe Metal
Pennsylvania	Lancaster	Lancaster Battery Company
	Lyon Station	East Penn Manufacturing
	Nesquehoning	Tonolli Corporation
	Reading	General Battery Corporation
Tennessee	College Grove	General Smelting and Refining
	Memphis	Refined Metals
	Rossville	Ross Metals, Inc.
Texas	Dallas	Dixie Metals/General Battery Corporation
	Dallas	Murph Metals/RSR Corporation
	Frisco	GNB Batteries/Gould, Inc.
	San Antonio	Standard Industries
Virginia	Richmond	Hyman Viener and Sons
Washington	Seattle	Quemetco/RSR Corporation

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

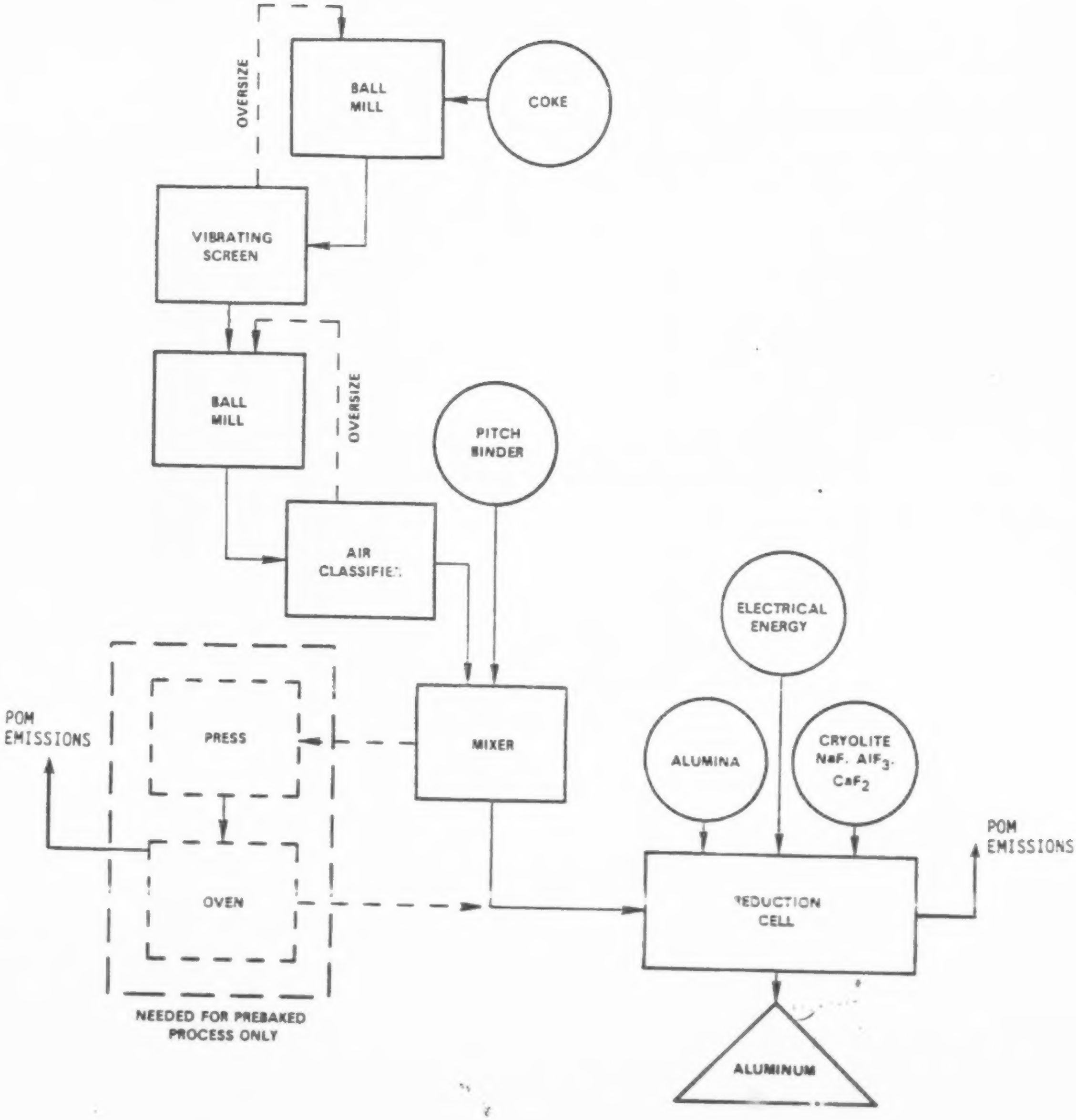

OVERSIZE
BALL MILL
COKE
VIBRATING SCREEN
BALL MILL
OVERSIZE
PITCH BINDER
AIR CLASSIFIER
ELECTRICAL ENERGY
POM EMISSIONS
PRESS
MIXER
ALUMINA
CRYOLITE NaF. AlF$_3$. CaF$_2$
POM EMISSIONS
OVEN
REDUCTION CELL
NEEDED FOR PREBAKED PROCESS ONLY
ALUMINUM

Figure 32. General flow diagram for primary aluminum production.[142]

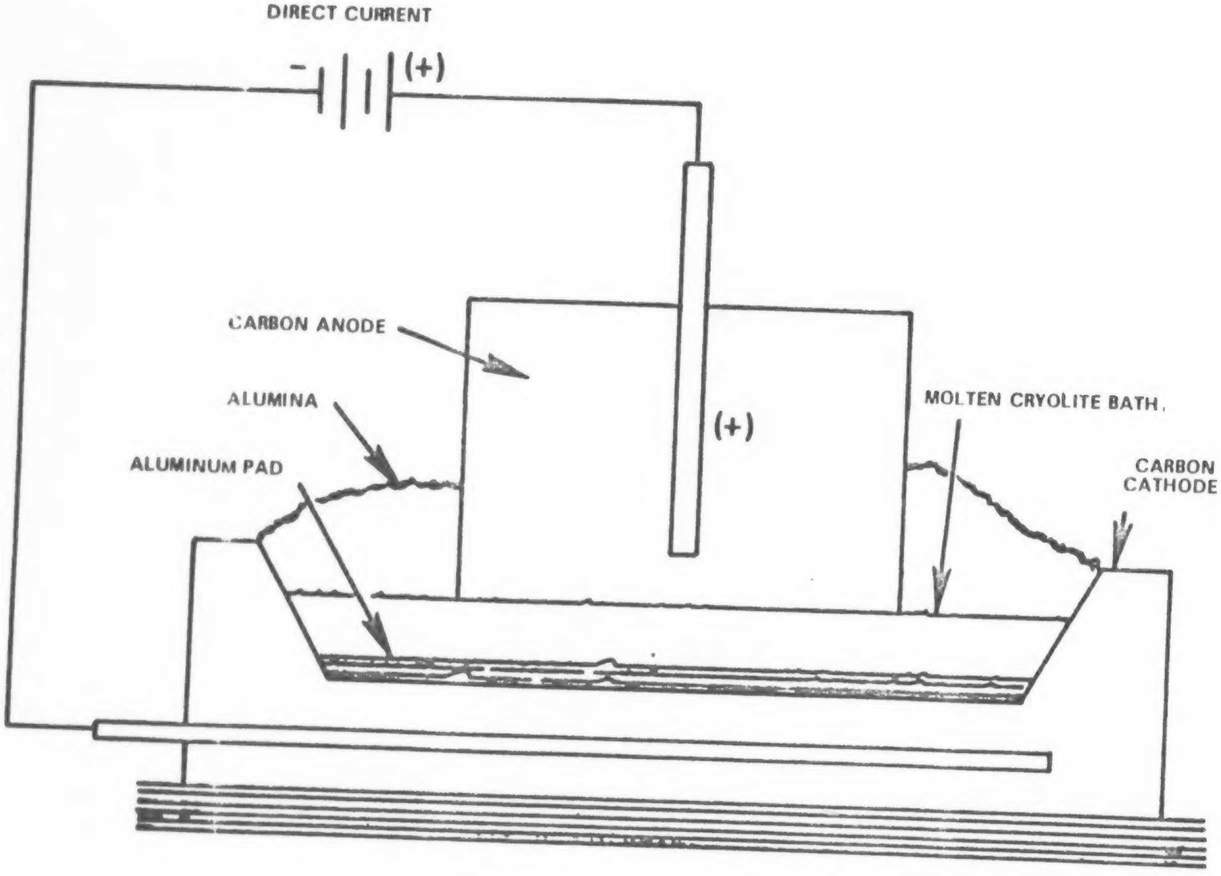

DIRECT CURRENT
-
(+)
CARBON ANODE
ALUMINA
ALUMINUM PAD
(+)
MOLTEN CRYOLITE BATH.
CARBON
CATHODE

Figure 33. Aluminum reduction cell diagram.[142]

Cryolite, a double fluoride salt of sodium and aluminum (Na_3AlF_6), serves as an electrolyte and a solvent for alumina. Alumina is added to and dissolves in the molten cryolite bath. The cells are heated and operated between 950 and 1000°C (1742 to 1832°F) with heat that results from resistance between the electrodes. During the reduction process, the aluminum is deposited at the cathode where, because of its heavier weight (2.3 g/cm^3 versus 2.1 g/cm^3), it remains as a molten metal layer underneath the cryolite. The cryolite bath thus also protects the aluminum from the atmosphere. The by-product oxygen migrates to and combines with the consumable carbon anode to form carbon dioxide and carbon monoxide, which continually evolve from the cell. The basic reaction of the reduction process is:[142]

$$Al_2O_3 + 1.5C \longrightarrow 2Al + 1.5CO_2$$

Alumina and cryolite are periodically added to the bath to replenish material that is removed or consumed in normal operation. The weight ratio of sodium fluoride (NaF) to aluminum fluoride (AlF_3) in cryolite is 1.5. Fluorspar (calcium fluoride) may also be added to lower the bath melting point.

Periodically, the molten aluminum is siphoned or tapped from beneath the cryolite bath, moved in the molten state to holding furnaces in the casting area, and fluxed to remove trace impurities. The product aluminum is later tapped from the holding furnaces and cast into ingots or billets to await further processing or shipped molten in insulated ladles.[142]

The process of primary aluminum reaction is essentially one of materials handling. The true difference in the various process modifications used by the industry lies in the type of reduction cell used. Three types of reduction cells or pots are used in the United States: prebake, horizontal stud Soderberg, and vertical stud Soderberg. Prebake cells constitute the bulk of aluminum production (66 percent), followed by horizontal Soderberg (21 percent), and vertical Soderberg (13 percent).[142]

Both Soderberg cells employ continuously formed consumable carbon anodes where the anode paste is baked by the energy of the reduction cell itself. The prebake cell, as indicated by its name, employs a replaceable, consumable carbon anode, formed by baking in a separate facility called an anode bake plant, prior to its use in the cell.

The preparation and operation of the aluminum reduction cells is the source of potential POM emissions from primary aluminum production. The magnitude of POM emissions from a typical reduction plant is a function of the type of reduction cell used.[143] Prebaked cell anodes are made by curing carbon contained in pitch and coke at relatively high temperatures [~1100°C (2012°F)]. A flow diagram depicting the production of prebaked cells is given in Figure 34. The high temperature curing process can potentially generate POM compounds.

Potentially, POM compounds can be emitted from the prebake cell during the reduction process when the anodes are lowered into the reduction pot. However, POM emissions from reduction are expected to be less than that from prebake cell preparation because the majority of POM emissions have already been released during the high temperature curing operation.[142,144] Data in Reference 144 support this theory.

Soderberg cell anodes are continuously lowered and baked by conductive heat from the molten alumina bath rather than being premolded and baked. A coke and coal tar pitch paste is packed into a metal shell over the bath. As the baked anode at the bottom of the shell is consumed, more paste is added at the top of the shell. As the paste is consumed, POM emissions are potentially released. Since the carbon paste is not baked prior to being placed in the pot, POM emissions from a Soderberg cell (horizontal or vertical stud) reduction operation would have the potential to be much greater than those from a prebaked cell reduction operation.

Emissions control at primary aluminum reduction facilities (cell rooms) is intended primarily for fluoride removal and involves efficient emissions capture and removal. Emissions capture is generally accomplished by using

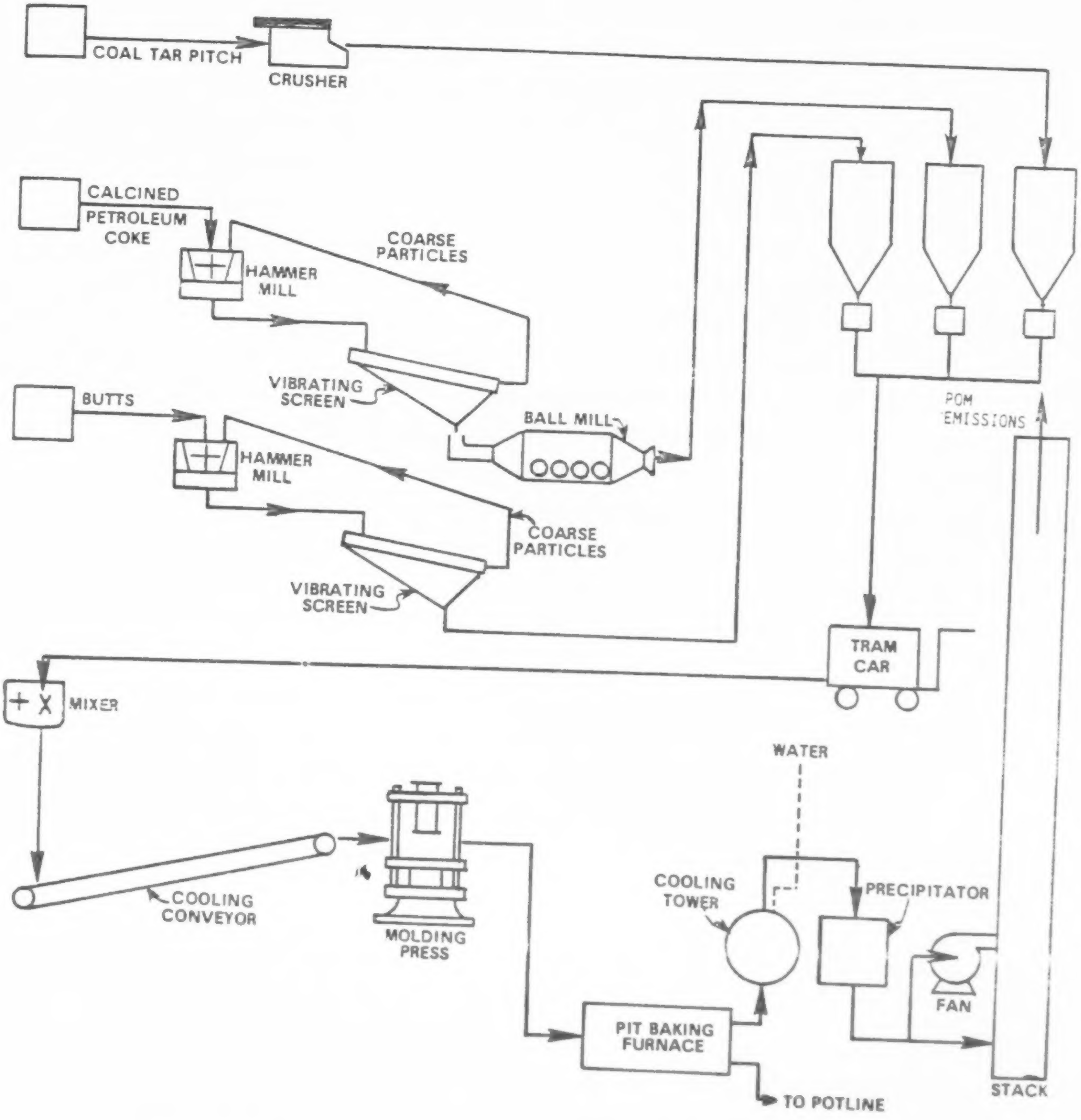

COAL TAR PITCH
CRUSHER
CALCINED
PETROLEUM
COKE
HAMMER MILL
COARSE PARTICLES
VIBRATING SCREEN
BUTTS
HAMMER MILL
BALL MILL
COARSE PARTICLES
VIBRATING SCREEN
POM EMISSIONS
TRAM CAR
MIXER
WATER
COOLING CONVEYOR
MOLDING PRESS
COOLING TOWER
PRECIPITATOR
FAN
PIT BAKING FURNACE
TO POTLINE
STACK

Figure 34. Flow diagram for the production of prebake anodes.[142]

precisely designed hooding and ducting systems on reduction cells. The term hooding includes the use of classical draft hoods and the use of movable doors, enclosures, and skirts. Primary emissions removal is achieved through the use of dry scrubbing systems or wet scrubber/electrostatic precipitator combination systems. Two types of dry scrubbing systems, fluidized bed and injected alumina, are found in that industry. Both forms of dry scrubbers contain baghouse equipment to collect particulate matter from the chemical absorption scrubbing process. These baghouses would be effective in removing particulate POM in the emission stream. Standard design spray tower wet scrubbers and wet electrostatic precipitators used in the series are also effective primary control systems at aluminum reduction facilities. The ability of the combination scrubbing/precipitation system to remove particulate POM should be equal to that of the dry scrubbing baghouses, and may exceed it because of the combination system's ability to control some vaporous POM compounds through gas cooling and subsequent particulate collection. In addition to being a primary control system for cell room emissions, the wet scrubber/ESP combination is also used as the primary control system for facilities producing prebake anodes.[142]

In some primary aluminum installations, secondary control systems are also used to augment the primary systems. The predominant secondary system is a spray screen scrubber followed by a mist eliminator. The term spray screen scrubber is applied to wet scrubbers in which the scrubbing liquor is sprayed into a gas stream and on to screens or open mesh filters enclosed in a plenum chamber.[142]

Emission Factors

One set of POM emissions data have been identified for aluminum smelting plants. Emissions of particulate and vaporous POM have been measured from an anode paste preparation process, a horizontal Soderberg reduction cell, and a vertical Soderberg reduction cell at a Swedish aluminum smelter.[145] The results of these source tests, as reported in the literature, are given in Table 69. As would be expected, the anode paste preparation process emissions have greater POM concentrations than either of

TABLE 69. POM EMISSION FACTORS FOR PRIMARY ALUMINUM SMELTING PLANTS[145]

Emissions Source	POM Emission Factor (mg/m³)[a] Filter Component	XAD-2 Component	Total	POM Emission Factor kg POM ton/Aluminum	Percent of Total POM Concentration That is Benzo(a)pyrene
Anode Paste Process					
- Pitch Melter[b,c]	1858	894	2752	Data not available	0.2
- Mixer[b]	447	128	575	Data not available	0
- Briquetting[b]	6.6	2.6	9.2	Data not available	0.3
Horizontal Soderberg Pot Room					
- Pot Gas Scrubber No. 1[d]	15.76	4.52	20.28	1.21	2.5
- Pot Gas Scrubber No. 2[d]	8.39	3.35	11.75	0.71	2.6
- Pot Gas Scrubber No. 3[d]	12.85	4.73	17.58	1.06	2.7
- Pot Gas Scrubber No. 4[d]	14.15	3.92	18.07	1.08	2.5
- Ventilation Air from Pot Rooms	0.19	0.11	0.30	0.34	2.4
- Total Horizontal Soderberg Room	---	---	---	4.4	2.5
Vertical Soderberg Pot Room					
- Pot Gas Dry Scrubber	0.002	0.035	0.037	0.001	0
- Ventilation Air Scrubber 1A[e]	0.063	0.313	0.376	0.036	2.1
- Ventilation Air Scrubber 2A[e]	0.035	0.222	0.257	0.018	1.5
- Ventilation Air Scrubber 4B[e]	0.146	0.776	0.922	0.105	1.0
- Ventilation Air Scrubber 4A[e]	0.064	0.382	0.446	0.020	1.7
- Ventilation Air Scrubber 5B[e]	0.165	0.442	0.607	0.036	1.5
- Average for All Ventilated Air from Vertical Soderberg Process	---	---	---	0.699	1.5
- Total Vertical Soderberg Room	---	---	---	0.7	1.5

---

[a] All concentrations are in terms of cubic meters of air at standard conditions.

[b] Uncontrolled source.

[c] The predominant POMs (by percent) measured in this source's emissions were naphthalene, fluoranthene, fluorene, anthracene, benz(e)acenaphthalene, and 2-methylnaphthalene.

[d] Cleaned pot gas was found to contain predominantly fluoranthene, benz(e)acenaphthalene, benz(b)fluoranthene, phenanthrene, anthracene, and benzo(j,k)fluoranthene.

[e] Closed ventilation air was found to contain predominantly anthracene, fluorene, naphthalene, fluoranthene, phenanthrene, and 2-methylfluorene.

the Soderberg processes. The test data in Table 69 illustrate that the majority of the POM emissions from the anode past process were particulate matter and not vapors. The POM emissions of the horizontal Soderberg process exhibit a similar behavior as evidenced by the Table 69 data. Conversely, POM emissions from the vertical Soderberg process were predominantly in vapor form instead of particulate.[145]

A list of all the POM compounds identified in emissions from the aluminum smelter is provided in Table 70.[145]

Source Locations

As of January 1985, there were 28 primary aluminum reduction plants in the United States operated by 10 different companies. Washington State has seven plants, the most of any State in the country. A complete list of all 29 facilities is given in Table 71.[146]

WOOD CHARCOAL PRODUCTION

Process Description

Charcoal, primarily used for outdoor cooking, is manufactured by the pyrolysis of carbonaceous raw materials, primarily medium to dense hardwoods such as beech, birch, maple, hickory, and oak. Softwoods, sawdust, nutshells, fruit pits, and vegetable wastes are also used in the pyrolysis process. The high temperature (450 to 510°C) pyrolysis of wood materials is a potential means of generating POM air emissions.[147]

Hardwood charcoal is manufactured by a four-step pyrolysis process. Heat is applied to the wood, and as the temperature rises to 100°C (212°F), water and highly volatile hydrocarbons are distilled off. The wood temperature remains at approximately 100°C until the moisture content of the wood has been removed, at which time the volume of distillate production declines and the wood temperature begins to climb. During the next stage,

TABLE 70. POM COMPOUNDS IDENTIFIED IN THE EMISSIONS OF A PRIMARY ALUMINUM SMELTER[145]

POM Compounds Measured in Aluminum Smelter Emissions[a]
1. Naphthalene
2. 2-Methylnaphthalene
3. 1-Methylnaphthalene
4. Biphenyl
5. Acenaphthylene
6. Acenaphthene
7. Fluorene
8. 2-Methylfluorene
9. 1-Methylfluorene
10. Phenanthrene
11. Anthracene
12. 3-Methylphenanthrene
13. 2-Methylphenanthrene
14. 2-Methylanthracene
15. 4,5-Methylenephenanthrene
16. 4- and/or 9-Methylphenanthrene
17. 1-Methylphenanthrene
18. Fluoranthene
19. Benz(e)acenaphthylene
20. Pyrene
21. Ethylmethylenephenanthrene
22. Benzo(a)fluorene
23. Benzo(b)fluorene
24. 4-Methylpyrene
25. 2-Methylpyrene and/or methylfluoranthene
26. 1-Methylpyrene
27. Benzo(c)phenanthrene
28. Benz(a)anthracene

TABLE 70. POM COMPOUNDS IDENTIFIED IN THE EMISSIONS OF A PRIMARY ALUMINUM SMELTER[145] (Continued)

POM Compounds Measured in Aluminum Smelter Emissions[a]
29. Chrysene and triphenylene
30. Benzo(b)fluoranthene
31. Benzo(j+k)fluoranthene
32. Benzo(e)pyrene
33. Benzo(a)pyrene
34. Perylene
35. Indeno(1,2,3-c,d)pyrene
36. Dibenz(a,c and/or a,h)anthracenes
37. Benzo(g,h,i)perylene

[a] Emission sources included anode paste preparation, a horizontal Soderberg pot room, and a vertical Soderberg pot room.

TABLE 71. LIST OF PRIMARY ALUMINUM PRODUCTION FACILITIES IN THE UNITED STATES IN 1985[146]

Facility	Location
Alumax, Inc.	Mount Holly, SC Frederick, MD Ferndale, WA
Aluminum Company of America	Alcoa, TN Badin, NC Massena, NY Rockdale, TX Vancouver, WA Warrick County, IN Wenatchee, WA
Atlantic Richfield Company	Columbia Falls, MT Sebree, KY
Consolidated Aluminum Corporation	New Johnsonville, TN
Kaiser Aluminum and Chemical Corporation	Chalmette, LA Mead, WA Ravenswood, WV Tacoma, WA
Martin Marietta Corporation	The Dalles, OR Goldendale, WA
National-Southwire Aluminum Company	Hawesville, KY
Noranda Aluminum, Inc.	New Madrid, MO
Ormet Corporation	Hannibal, OH
Reynolds Metals Company	Arkadelphia, AR Jones Mill, AR Longview, WA Massena, NY Sheffield, AL Troutdale, OR

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

the wood temperature rises with heat input to approximately 275°C (527°F), and hydrocarbon distillate yield increases. As the third stage begins in the vicinity of 275°C, external application of heat is no longer required since the carbonization reactions become exothermic. During this stage, the wood temperature rises to 350°C (662°F), and the bulk of hydrocarbon distillates are produced. At approximately 350°C, exothermic pyrolysis ends, and during the final stage, heat is again applied, raising the wood temperature to 400 to 500°C (752 to 932°F) to remove more of the less volatile, tarry materials from the product charcoal.

Currently, there are predominantly two types of vessels used to manufacture wood charcoal, the Missouri-type batch kiln and the continuous Herreshoff furnace. The batch process and kiln account for about 45 percent of national wood charcoal production. The Missouri-type kiln shown in Figure 35 is typically constructed of concrete.[148] A Missouri-type batch kiln normally processes about 45 to 50 cords of wood in a 10- to 25-day cycle. A typical cycle may be structured as follows.

1 - 2 days	load wood
5 - 8 days	pyrolysis
10 - 14 days	cool
1 - 2 days	unload charcoal

After the wood is manually loaded in the kiln, a fire is started, usually at the bottom center of the kiln, by igniting easily combustible materials placed at this point during the loading. During ignition, a large amount of air is necessary for the rapid combustion of the starting fuels to insure the heat level needed for pyrolysis. This air is supplied through groundline ports in the kiln side walls or through temporary openings under the kiln door. In some cases, the kiln doors remain open until the burn is adequately started. Auxiliary ceiling ports in some kilns serve as temporary stacks and aid ignition by causing greater amounts of air to be drawn into the kiln through the air ports. They also aid removal of smoke from the kiln.[148]

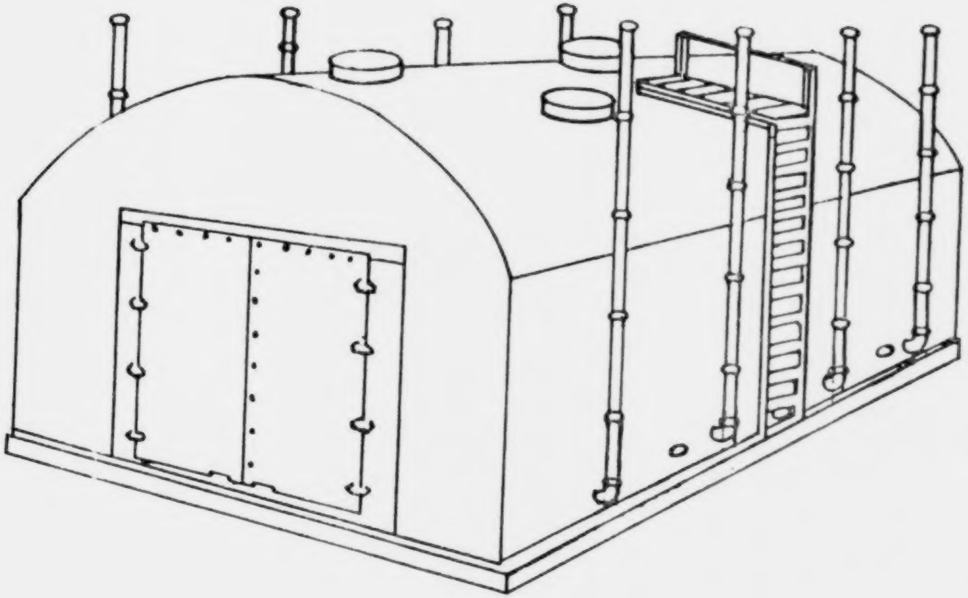


Figure 35. Missouri-type charcoal kiln.[148]

Ignition patterns are generally similar for all types of kilns. During the first 5 to 15 minutes, temperatures in the ignition area will rise rapidly to about 540°C (1004°F). After much of the fuel has been burned, the temperatures will quickly drop, often to as low as 150°C (302°F). The extent of the temperature drop is closely related to conditions of air supply and to the moisture content of the charge. With the establishment of a suitable ignition zone, however, the temperature gradually increases to about 280°C (536°F), and the ignition period is considered complete.[148]

Satisfactory carbonization depends primarily on the maintenance of proper burning conditions in the pyrolysis zone. Sufficient heat must be generated first to dry the wood and then to maintain temperatures necessary for efficient carbonization. At the same time, the burning must be limited so that only sufficient heat is present to produce good charcoal. Temperature control is attained by varying the size of the air port openings providing air for combustion of wood volatiles.[148]

For the production of good-quality charcoal, kiln temperatures from about 450 to 510°C (842 to 950°F) are required. Prolonged higher temperatures will reduce the yield of charcoal without necessarily upgrading it for recreational use. If, on the other hand, pyrolysis temperatures remain low, the charcoal may be too smoky for domestic use, and larger than normal amounts of brands (partially charred wood) will be produced.[148]

The direction and rate of spread of the pyrolysis zone is associated with a number of factors, such as location of air ports and stacks, volume and velocity of the incoming air, wood size and moisture content, piling of the charge, and design of the kiln. Pyrolysis generally proceeds at a faster rate at the upper part of the charge, where higher temperatures are available for longer periods of time. Less rapid pyrolysis takes place near the kiln floor, where the average temperature usually is lowest. In the Missouri-type kiln, combustion and carbonization progresses from the top of the kiln to the floor and from the center to the walls.[148]

Burn progress can be determined by the color of the smoke from the kiln or by determining the temperature along the vertical distance of the steel doors. The pyrolysis is completed when fire has reached the floor of the kiln as determined by view ports (air intake ports) at the floor level. This may also be indicated by a marked decrease in the volume of smoke and a color change from grayish yellow to bluish white.[148]

When pyrolysis has been completed, all air ports are sealed for the start of the cooling cycle. After the ports are sealed, the stacks remain open until smoking has practically stopped to prevent the development of gas pressure in the kiln. Stacks can usually be sealed from 1 to 2 hours after the air ports are closed. The kiln is allowed to cool for about 10 to 14 days before removing the charcoal. Yields of approximately 25 percent are achieved.[148]

The required pyrolysis time and resultant POM emissions from a Missouri-type batch kiln vary with kiln capacity, operational practices, wood type, and wood moisture content. Process reaction gases containing POM are exhausted from the kiln in stacks that run along the side walls of the vessel.[147,148] The charcoal product of a batch kiln process is either sold directly or made into briquettes prior to selling.

Continuous charcoal production is accomplished in Herreshoff multiple hearth furnaces. The use of continuous multiple hearth units for charcoal production has increased because of the following advantages of the units.

- Lower labor requirements than kiln operations where manual loading and unloading is needed. Only one man per shift is required for continuous facilities.
- Consistent yield and quality charcoal with easy control of product volatile and fixed carbon content.
- Feed of multiple forms of wood waste.
- Off-gases easily collected for further processing.

The typical feedstock capacity of continuous wood charcoal furnaces is 2.5 Mg (2.75 tons)/hour.

The operational principles of the Herreshoff furnace (shown in Figure 36) are relatively simple. Passing up through the center of the furnace is a shaft to which are attached two to four rabble arms for each hearth. As the shaft turns, the hogged wood material resting on the hearth floors is continually agitated, exposing fresh material to the hot gases being evolved. A further function of the rabble arms is to move material through the furnace. On alternate hearths, the teeth are canted to spiral the material from the shaft toward the outside wall of the furnace or from the outside wall toward the center shaft. Around the center shaft is an annular space through which material drops on alternate hearths, while on the remaining hearths material drops through holes in the outer periphery of the hearth floor. In this way, material fed at the top of the furnace moves alternately across the hearths at increasing temperatures until it discharges from the floor of the bottom hearth. Charcoal exiting from the furnace is cooled by water sprays and water jacketing on a cooler. These sprays are controlled automatically by a temperature regulator set for a given charcoal temperature. As with batch kilns, the charcoal product of continuous kilns is either sold directly or further processed to briquettes for sale.[148]

Initial heat for startup is provided by oil- or gas-fired burners mounted in the sides of the hearths. When furnace temperature has been attained, the auxiliary fuel ceases, and combustion air is used to ignite the evolving wood gases to maintain furnace temperature. Furnace temperatures range between 480 and 650°C (896 to 1202°F). Exhaust gases from the charcoal production process are vented to the atmosphere or to controls through stacks located on top of the furnace, are used as a heat source for predrying of feed material and drying of briquettes produced at an adjacent vessel, or are burned in a waste heat boiler to produce steam.[147]

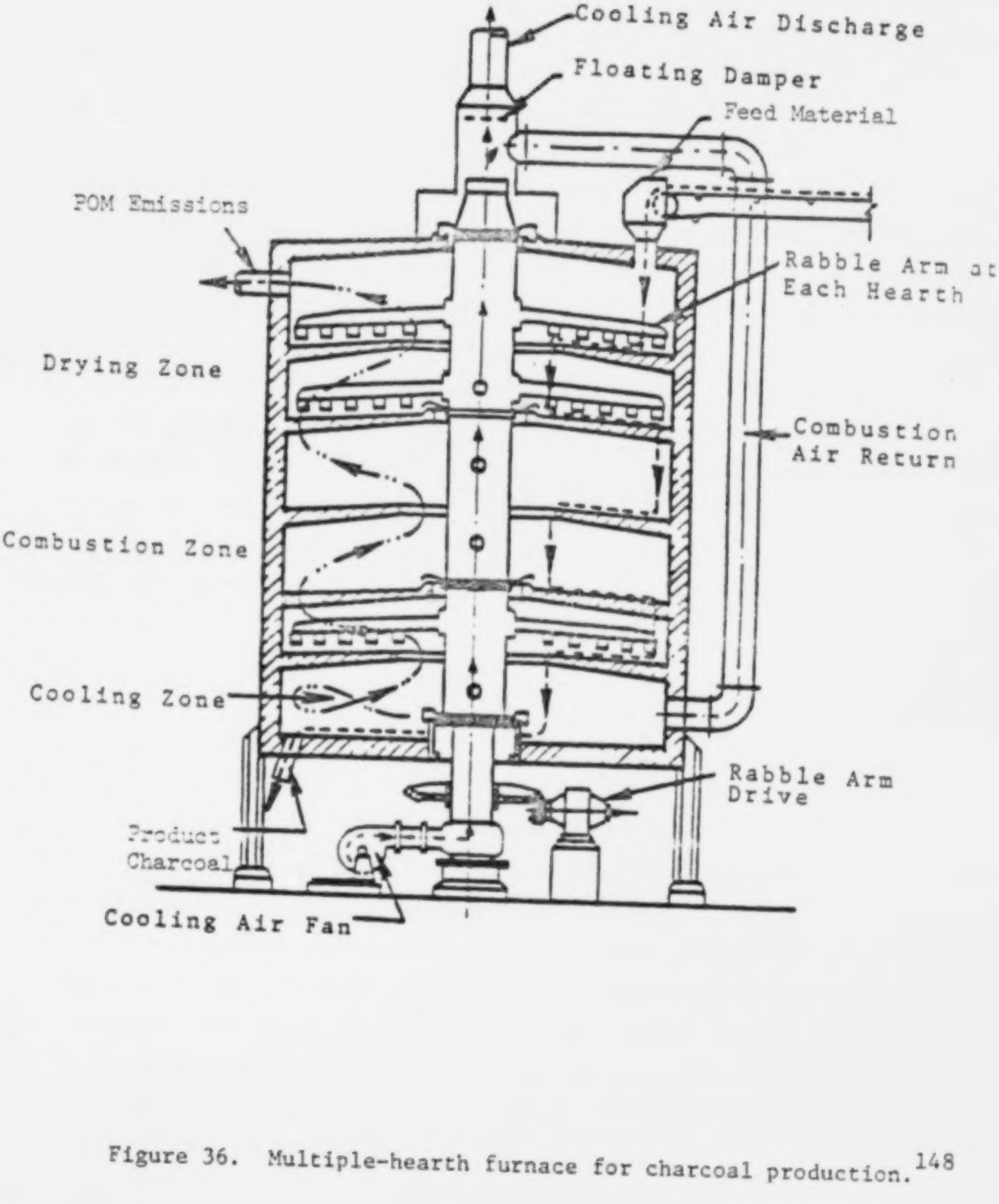

Cooling Air Discharge
Floating Damper
Feed Material
POM Emissions
Rabble Arm at Each Hearth
Drying Zone
Combustion Air Return
Combustion Zone
Cooling Zone
Rabble Arm Drive
Product Charcoal
Cooling Air Fan

Figure 36. Multiple-hearth furnace for charcoal production.[148]

A 1978 U. S. EPA investigation into wood charcoal production indicated that many of the batch kilns are relatively old and many, particularly smaller kilns, are uncontrolled.[147,148] In general, the control of emissions, including POM, from batch wood charcoal kilns is complicated by the cyclical nature of the process. Throughout the cycle, both emission composition and flow rate change. Direct-fired afterburners for the destruction of hydrocarbons have been suggested to be the most feasible control system; however, these devices would require an auxiliary fuel such as natural gas. Economic analyses have indicated that for typical batch kilns, the operation of afterburners for emissions control would cause firms to lose money.[148] With the combustion of auxiliary fuel of any type, a potential is also created for additional POM emissions. No information is available on the proportion of batch kilns with afterburner controls or the effect of afterburner use on POM emissions.[147]

Continuous wood charcoal furnaces are predominantly controlled by direct-fired afterburners.[147,148] Auxiliary fuel firing is required in continuous furnace afterburners only during start-up or process upsets because of the generally higher heating value of continuous furnace exhaust gases. One facility has been found to be using an incinerator to control furnace emissions.[148]

Emission Factors

Polycyclic organic matter emission factor data are available in the literature only for a Missouri-type batch kiln.[147] Five sampling runs were made and total uncontrolled POM emissions averaged 3.5 g/Mg (0.007 lb/ton) of charcoal produced. Reference 147 indicates that the POM samples from these tests were obtained using a modified Method 5 procedure and sample analysis was performed by gas chromatography. Benz(c)phenanthrene and benzo(a)pyrene were identified as constituents of total POM emissions. Four other POM compounds, dibenz(a,h)anthracene, 3-dimethylcholanthrene, 7,12-dimethylbenz(a)anthracene, and 3,4,5,6-dibenzocarbazole, were specifically analyzed for but were not detected in any of the samples.[147]

The authors of Reference 147 noted that the results of the batch kiln emission tests might be of questionable value due to the difficulty of sampling the kiln and "the improvisational sampling techniques" used. No estimate of the accuracy of the test results was provided.

Source Locations

Wood charcoal manufacturing facilities are located in 24 States primarily in Missouri, Arkansas, and in several southeastern States.[148] A list of wood charcoal producers in the United States is provided in Table 72.[148]

CREOSOTE WOOD TREATMENT

Process Description

Creosote impregnation plants, also called wood treatment plants, have been identified as potential air emission sources of POM because creosote contains significant quantities of POM compounds. Creosote is a product of the fractional distillation of coal tar, which is a by-product of bituminous coal coking. The principal use of creosote is as a wood preservative. It is used to treat crossties, switch ties, utility poles, crossarms, marine and foundation pilings, construction lumber, fence posts, and plywood.[144]

Treatment is accomplished by either pressure or non-pressure processes. To initiate either process, wood products are debarked and conditioned. Conditioning, primarily moisture removal, is performed by air seasoning or kiln drying in the majority of plants. Depending on the particular preservative to be applied, conditioning may also be performed by steaming the wood in the treatment retort, heating the wood in oil under reduced pressure, or exposing it to hot vapors of organic solvents (vapor drying). To expedite certain treatment processes, the wood may be pierced by knives (a process called incising) to provide avenues for penetration of the preservative solutions.[149]

TABLE 72. CHARCOAL PRODUCERS IN THE UNITED STATES[148,a]

State	City or County	Producer
Alabama	Dothan	Kingsford Company
	Tuscumbia	Malone Charcoal Company
	Muscle Shoals	McKinney Lumber and Plywood
Arkansas	Jasper	Jasper Charcoal Company
	Huntsville	Keeter Charcoal Company
	Omaha	Keeter Charcoal Company
	Green Forest	Keeter Charcoal Company
	Yellville	Martin Charcoal Company
	Paris	Ozark Charcoal Company
	Scranton	Scranton Charcoal Company
	Waldron	Waldron Charcoal Company
	Harrison	Newberry Charcoal Company
	Paris	Paris Charcoal Company
	Paris	Arkansas Charcoal Company
	Hot Springs	Weyerhaeuser Company
	George	George Charcoal Company
	Hatfield	Arkansas Charcoal Company
	Waldron	Waldron Charcoal Company
	Mountain View	Hinesley and Everett Enterprises
California	Elk Grove	C. B. Hobbs Corporation
	Santa Clara	C. B. Hobbs Corporation
	Milipitas	C. B. Hobbs Corporation
Florida	Ocala	Pioneer Charcoal
Georgia	Atlanta	Husky Industries
Kansas	Chetopa	Jayhawk Charcoal Company
Kentucky	Burnside	Kingsford Company
Illinois	Chicago	Great Lakes Carbon Corporation
Maryland	White Church	Kingsford Company
	Oakland	Kingsford Company
Minnesota	Isanti	Husky Briquetting, Inc.
Mississippi	Bruce	Blackjack Charcoal Company
	Pachuta	Hood Charcoal Company
	Pachuta	Masonite Corporation, Charcoal Division
	Beaumont	Ronnies Hickory Chips

[a] In 1978

TABLE 72. CHARCOAL PRODUCERS IN THE UNITED STATES[148] (Continued)

State	City or County	Producer
Missouri	Barry	Harris Enterprises
	Purdy	Heaser Charcoal Company
	Boone	Charles Chrisman Charcoal
	Centralia	L and A Dailing Charcoal Company
	Carter	Big Springs Industrial
	Carter	Carter County Charcoal
	Ellsinore	Leach Brothers Charcoal
	Ellsinore	Rozark Farms
	Van Buren	Big Springs Charcoal
	Van Buren	Big Springs Charcoal
	Cole	Stegeman Charcoal Company
	Henley	Louis Stegeman Charcoal Company
	Jefferson City	Rich Stegeman Charcoal Company
	Steelville	Hardwood Charcoal Company
	Wesco	Fordell Development Corporation
	Greenfield	Pringle Charcoal Company
	Salem	Carty Charcoal
	Salem	Floyd Charcoal Company
	Salem	C and H Charcoal
	Dent	Langworthy Charcoal Company
	Dent	Lennox Charcoal Company
	Salem	Wieberg Charcoal Company
	Salem	Hobson Charcoal Company
	Gasconade	Hickory Charcoal Company
	Owensville	Gene's Charcoal
	Wheatland	J and E Charcoal Company
	Howell	Missouri Charcoal Company
	Mount View	Craig Charcoal Company
	West Plains	Nubbin Ridge Charcoal Company
	Mount View	Bays Sawmill and Charcoal
	Peace Valley	Peace Valley Kilns
	Mount View	Old Hickory Charcoal Company
	Mount View	Carr Forest Products
	Kansas City	Standard Milling Company
	Hocomo	Bakersfield Charcoal Company
	Laclede	Independent Stave Company
	Laclede	Timber Products Company
	Vienna	Wulff Charcoal Company
	High Gate	Kingsford Company
	Belle	Kingsford Company
	Belle	W. B. Stockton
	Belle	H and D Charcoal
	Hayden	Curtis and Hayes Charcoal
	Iberia	Louis Stegeman Charcoal

TABLE 72. CHARCOAL PRODUCERS IN THE UNITED STATES[148] (Continued)

State	City or County	Producer
Missouri (continued)	Miller	Kalaf Charcoal
	St. Elizabeth	Kirkweg Charcoal Company
	Neosho	Neosho Charcoal Products
	Oregon	Greer Springs Company
	Meta	Barnhart Charcoal
	Osage	J and M Charcoal Company
	Osage	Kelly Charcoal Company
	Freeburg	Al Luecke Charcoal Company
	Osage	McDonald Charcoal Company
	Osage	Ridenhour Charcoal Company
	Meta	Ripka Charcoal and Lumber
	Osage	Sugar Creek Charcoal Company
	Freeburg	Wieberg Charcoal Company
	Freeburg	Ben Berhorst
	Meta	Charkol, Inc.
	Belle	Gene Noblett Charcoal Company
	Meta	Standard Milling Company
	Gainesville	Ozark Forest Charcoal
	Ozark	Wallace Charcoal Company
	St. James	Parry Charcoal Company
	Lake Spring	Lenox Charcoal
	Vienna	Tackett Charcoal Company
	Lesterville	Black River Charcoal Company
	Reynolds	Copeland Charcoal Company
	Winona	Dailey Charcoal
	Shannon	George Helmuth Charcoal
	Shannon	Royal Forest Charcoal
	Birch Tree	Kerr Charcoal
	Summersville	Craig Charcoal
	Round Springs	Roaring Springs Corporation
	Round Springs	Round Springs Charcoal
	Round Springs	Robert Hamilton
	Gladden	Timber Charcoal Company
	Branson	S and S Charcoal Company
	Bradleyville	Horner Charcoal Company
	Branson	Keeter Charcoal Company
	Raymondville	Thomason Charcoal Company
	Licking	Wulff Charcoal Company
	Plato	H. O. Charcoal Company
	Seymour	Oak-lite Corporation
	St. Louis	Cupples Company, Manufacturers
New Jersey	Teterboro	Degussa, Inc.

TABLE 72. CHARCOAL PRODUCERS IN THE UNITED STATES[148] (Continued)

State	City or County	Producer
North Dakota	Dickinson	Husky Industries
Ohio	Oak Hill	Victory Charcoal Company
	Lucas	Sun Oil Company
	West Marion	Great Lakes Carbon
	McArthur	Roseville Charcoal
Oklahoma	Heavener	Forest Products Charcoal Company
	Talihina	Forest Products Charcoal Company
	Clayton	Forest Products Charcoal Company
	Talihina	Talihina Charcoal Company
	Bull Hollow	Cherokee Forest Industries
Oregon	Springfield	Kingsford Company
	White City	Georgia Pacific Corporation
Pennsylvania	Brookville	Humphrey Charcoal
South Carolina	Lake City	T. S. Ragsdale Company, Inc.
Tennessee	Jamestown	Royal Oak Charcoal Company
	Red Bank	Cumberland Kingsford
	Cookeville	Royal Oak Charcoal Company
	Tullahoma	Tennessee Dickel Distilling
	Red Boiling Springs	Cumberland Charcoal Corporation
	Spencer	Royal Oak Charcoal Company
	Memphis	Arkansas Charcoal Company
	Lynchburg	Jack Daniels Distillery
Texas	Flatonia	B and B Charcoal
	Houston	Pine-O-Pine Company
	Jacksonville	Campfire Charcoal Company
	Jacksonville	Char Time Charcoal
	San Antonio	National Charcoal Company
Virginia	Kenbridge	Imperial Briquet Corporation
West Virginia	Belington	Kingsford Charcoal
	Beryl	Kingsford Charcoal
	Maysville	Kingsford Charcoal
	Parsons	Kingsford Charcoal
	Swiss	Roseville Charcoal
	Bentree	Roseville Charcoal

TABLE 72. CHARCOAL PRODUCERS IN THE UNITED STATES[148] (Continued)

State	City or County	Producer
Wisconsin	Hixton	Husky Industries

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

Pressurized processes are used to preserve 95 percent of all treated wood. These processes involve the application of pneumatic or hydrostatic pressure to expedite the movement of preservative liquid into wood. In the normal application of preservatives (e.g., creosote), wood is first loaded on trams and introduced into the pressure vessel. Once in the pressure vessel, wood can be creosote pressure treated by either the full-cell or the empty-cell process.[149]

In the full-cell process, an initial vacuum is applied to the charge for a period of about 30 minutes. At the end of this period, and while still maintaining the vacuum, the vessel is filled with creosote. The vacuum is then released and pressures of 50 to 250 psi are applied to the system. Pressure is maintained until the required gross absorption of preservative has been achieved. At the end of the pressure cycle, the pressure is reduced to atmospheric levels and the preservative liquid in the vessel is returned to storage. The treated wood will often be subjected to a final vacuum to remove excess preservative on the surface of the wood. Once completed, the vacuum is released, the door of the vessel is opened, and the treated stock is removed. Creosote retentions achieved by the full-cell process vary from 320 to 480 kg/m^3 (20 to 30 lbs/ft^3).[149]

In the empty-cell process, the treatment retort is filled with preservative while either at ambient pressure conditions or under an initial air pressure of 15 to 75 psi. The remainder of the treating process is the same as that described for the full-cell process. Depending on the specifications of the customer, wood preservative retentions achieved by the empty-cell process range from 96 to 208 kg/m^3 (6 to 12 lbs/ft^3).[149]

In both the full-cell and empty-cell processes, creosote may be applied in an undiluted form or diluted with coal tar or petroleum. Temperatures of application for creosote and its solutions range from 99 to 110°C (210 to 230°F).

Products such as marine pilings are always treated by the full-cell process. Utility poles, crossties, and fence posts are routinely treated by the empty-cell process. The amount of preservative retention needed and the treatment process required are determined by the biological hazard to which the treated wood will be subjected in service.

Non-pressurized wood treatment processes are used both commercially and by individual consumers for home, farm, and garden wood preservation. Generally, wood treated by non-pressure processes must be seasoned to a moisture content of 30 percent or less prior to treatment to provide the best results.[149]

Most commercial non-pressure creosote treatments are applied by cold-soak or thermal processes. In both processes, wood is exposed to the preservative in an open vessel. The principle behind the cold-soak process simply entails soaking seasoned wood in the preservative for a fixed period of time, or until a predetermined gross retention has been achieved. The thermal process involves exposing wood to hot creosote for 6 to 12 hours followed by exposure to the preservative at ambient temperature for 2 hours.[149]

Home and other non-commercial creosote treatments are typically performed by brush, dip, or spray methods. In these cases, creosote or creosote-based solutions are manually applied at ambient conditions to wood and allowed to dry. The amount of retention that is achieved is a function of wood type, wood moisture content, and wood porosity.[149]

The creosote wood treatment source category appears to a source of primarily fugitive POM emissions that are associated with the actual treatment process and the handling of creosote raw materials and treated products. Fugitive emissions from treatment occur when the treatment vessel is opened at the end of the cycle. The duration of such emissions from each vessel is relatively short because vessels are only opened once or twice during each working shift.[144,150]

A second source of fugitive POM emissions is during creosote transfer from an incoming tanker or rail car to plant storage facilities. The method and frequency of delivery is a function of plant size and location. Generally, the larger the facility the more and greater the creosote loads will be. Increased frequency and quantity means increased potential for emissions. Transfer of the preservative, whether from rail car or tanker, is normally accomplished using a closed piping system. In such a system, the greatest chance for fugitive emissions is at the origin where creosote is leaving the tanker or rail car and at the end of the transfer where creosote is entering the storage vessel.[144,150]

A third potential source of fugitive emissions of POM compounds from creosote wood treatment plants is evaporative losses from treated wood. If treated products are stored in a building, emissions of this type would be largely confined and would not be released to the outside air.[144,150]

No information concerning currently used or potential control equipment for POM emissions from creosote treatment processes was identified in the literature.

Emission Factors

No POM emissions or emission factor data were found in the literature for creosote impregnation plants. The existence of POM emissions in these facilities has been indicated by area samples of air in and around the plants and by personal breathing zone air samples that contained POM compounds. These samples were taken to assess worker exposure to POM compounds. In one facility, worker breathing zone samples had a benzo(a)pyrene range of 0.80 to 84 ug/m^3.[144] An area sample at the impregnation vessel had a benzo(a)pyrene content of 3.6 ug/m^3.[144] Both of these benzo(a)pyrene data points represent collected particulate matter only.

At a second creosote impregnation facility, personal breathing zone air samples were taken to measure both particulate and gaseous POM compounds. Breathing zone samples associated with handling creosote treated railroad ties contained a total POM concentration of 981.2 ug/m^3, of which 97 percent was collected as gaseous POM.[150] These results imply that gaseous POM emissions from treatment plants may be greater than particulate POM releases, and that creosote plants with only particulate POM levels may be greatly underestimating actual POM concentrations in plant air. These implications should be taken into consideration when attempting to estimate emissions from a creosote wood treating process.

Source Locations

Creosote wood treatment plants are located across the country, but they are predominantly found in the Southeast. Information compiled by the American Wood-Preservers Association and the American Wood Preservers Institute indicates that there are roughly 185 creosote treatment plants nationwide. A list identifying these facilities is given in Table 73.[151]

OIL SHALE RETORTING

Process Description

Oil shale retorting has been identified in the literature as a POM emissions source category. Retorting produces POM emissions because it involves high temperature contact with hydrocarbons and hydrocarbon-containing rock and because hydrocarbon-containing off-gases from retorting are typically incinerated.[152,153] Oil shale retorting is performed by two major processes, above-ground or surface retorting and below-ground or in situ retorting. In surface retorting, oil shale is mined and brought to the surface, crushed, and heated either externally or internally to extract oil from the shale rock. In externally heated operations, an external furnace is used to continuously apply heat to the shale retort. In an internally heated system, the oil shale furnishes its own heat because part of its organic matter is burned inside the retort.

TABLE 73. LIST OF CREOSOTE WOOD IMPREGNATION PLANTS IN THE UNITED STATES[151,a]

Company	Location
Acme Wood Preserving, Inc.	Princeton, WV
Alabama Wood Treating Corporation	Mobile, AL[a]
American Creosote Works, Inc.	Pensacola, FL Jackson, TN[a] Louisville, MS
American Wood Division of Powe Timber Company	Richton, MS
Annadale Plantation	Georgetown, SC
Appalachian Timber Services, Inc.	Sutton, WV White Plains, KY
Arizona Pacific Wood Preserving	Eloy, AZ
Atlantic Wood Industries, Inc.	Portsmouth, VA Hainesport, NJ Port Wentworth, GA
B and M Wood Products, Inc.	Manor, GA
Baldwin Pole and Piling Company	Bay Minette, AL
Baxley Creosoting Company, Inc.	Baxley, GA
J. H. Baxter and Company	The Dalles, OR Eugene, OR Weed, CA Laramie, WY
Benton Creosoting Works	Benton, LA
Birmingham Wood Preserving Company	Birmingham, AL
Broderick Wood Products Company	Denver, CO
Brown Wood Preserving Company, Inc.	Brownville, AL Louisville, KY
Burke-Parsons-Bowlby Corporation	Stanton, KY Dubois, NV Goshen, VA Spencer, WV
Burlington Northern, Inc.	Brainerd, MN Paradise, MT Somers, MT
Cahaba Pressure Treated Forest Products	Brierfield, AL

[a] In 1984

TABLE 73. LIST OF CREOSOTE WOOD IMPREGNATION PLANTS IN THE UNITED STATES[151] (Continued)

Company	Location
Carolina Creosote Corporation, Inc.	Leland, NC
Carolina Wood Preserving Company, Inc.	Scotland Neck, NC
Cascade Pole Company	Tacoma, WA[a]
Century Forest Industries	Lufkin, TX
Champion International Corporation	Cass Lake, MN Whitewood, SD
Colfax Creosoting Company	Pineville, LA
Conroe Creosoting Company	Conroe, TX
F. E. Cooper Lumber Corporation	Johnstown, PA
Crown Zellerback Treated Wood Products	Urania, LA Gulfport, MS
Dant and Russell, Inc.	North Planes, OR
Duke City Lumber Company	Livingston, TX
Dura-Wood Treating Company	Alexandria, LA
Easterday Tie and Timber Company	Jackson, TN
El Dorado Pole and Piling Company, Inc.	El Dorado, AR
Eppinger and Russell Company	Chesapeake, VA Brunswick, GA Brookhaven, FL
Escambia Treating Company	Camilla, GA
Evr-Wood Treating Company, Inc.	Jennings, LA
Fernwood Industries	Fernwood, MS
Florida Fence Post Company, Inc.	Ona, FL
Fordyce Wood Preservers	Fordyce, AR
Frank Brooks Manufacturing Company	Billingham, WA
G. C. L. Tie and Treating Corporation	Sidney, NY
Garland Creosoting Company	Longview, TX
Gateway Forest Products, Inc.	Mather, PA
General Timber, Inc.	Sanford, NC

TABLE 73. LIST OF CREOSOTE WOOD IMPREGNATION PLANTS IN THE UNITED STATES[151] (Continued)

Company	Location
Mixon Brothers Wood Preserving, Inc.	Idabel, OK
Moultrie Wood Preserving Company	Moultrie, GA
New South Forest Industries	Red Hill, SC
Osser Company	Bellingham, WA
Oliver Treated Products Company, Inc.	Hammond, LA
Ouachita-Nevada Treating Company	Reader, AR
Pacific Wood Preserving of Bakersfield	Bakersfield, CA
Pacific Wood Treating Corporation	Ridgefield, WA
Pearl River Wood Preserving Corporation	Picayune, MS
Perma Treat Corporation	Durham, CT
Prentiss Creosote and Forest Products, Inc.	Prentiss, MS[a]
R and K Creosote Company, Inc.	Natalbany, LA
Reddell Creosoted Forest Products, Inc.	Reddell, LA
San Diego Wood Preserving	National City, CA
Santa Fe Centralized Tie Plant	Somerville, TX
Seaman Timber Company, Inc.	Montevallo, AL
Sheridan Pressure Treating Lumber	Sheridan, OR
Shollenbanger Wood Treating	Bernalilco, NM
W. J. Smith Wood Preserving Company	Denison, TX
Southern Pine Wood Preserving Company	Wiggins, MS
Southern Wood Piedmont Company	Augusta, GA Baldwin, FL Chattanooga, TN East Point, GA Gulf, NC Macon, GA Spartanburg, SC Waverly, OH Wilmington, NC
Stallworth Timber Company, Inc.	Beatrice, AL
Standard Wood Preservers of Shreveport, Inc.	Shreveport, LA[a]

TABLE 73. LIST OF CREOSOTE WOOD IMPREGNATION PLANTS IN THE UNITED STATES[151] (Continued)

Company	Location
St. Regis Paper Company	Cass Lake, MN Whitewood, SD
Superior Tie and Timber	Vivian, LA
Superior Wood Treating, Inc.	Louisville, MS
Sweeney Wood Products	Lapoint, UT[b]
J. C. Taylor Lumber Sales	Sheridan, OR
Texarkana Wood Preservative Company	Texarkana, TX
Texas Electric Cooperatives, Inc.	Jasper, TX
Thompson Industries	Russellville, AR
Thomasson Lumber Company	Philadelphia, MS
Timco, Inc.	Wiggins, MS
Union Lumber Company	Homerville, GA
Utah Power and Light	Idaho Falls, ID
Vermont Correctional Industries	Windsor, VT
Virginia Wood Preserving	Laurel, VA
Webster Wood Preserving Company	Bangor, WI
Western Tar Products Corporation	Terre Haute, IN
Western Wood Preserving Company	Sumner, WA
Wood Preservers, Inc.	Warsaw, VA
Wood Treating, Inc.	Picayune, MS
Wyckoff Company	Bainbridge Island, WA Seattle, WA

---

[a] Plants use non-pressure treating techniques in addition to pressure treating processes.

[b] Plants use only non-pressure treating processes.

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

TABLE 73. LIST OF CREOSOTE WOOD IMPREGNATION PLANTS IN THE UNITED STATES[151] (Continued)

Company	Location
General Wood Preserving Company, Inc.	Leland, NC
Glacier Park Company	Somers, MT
Glenville Wood Preserving Company, Inc.	Glenville, GA
Great Lake Timber Company	Ft. Duschene, UT
Hart Creosoting Company	Jasper, TX
Huxford Pole and Timber Company, Inc.	Huxford, AL
Holcomb Creosote Company	Yadkinville, NC
Hoosier Treating Company	Gosport, IN
Indiana Wood Treating Corporation	Bloomingdale, IN
International Paper Company	De Ridder, LA Joplin, MO Longview, WA Navasota, TX[a] Wiggins, MS
Jasper Creosoting Company	Jasper, TX
Jennison-Wright Corporation	Granite City, IL Toledo, OH
Joslyn Manufacturing and Supply Company	Richton, MS
Julian Lumber Company	Antlers, OK
Kerr-McGee Chemical Corporation	Avoca, PA Indianapolis, IN Kansas City, MO Madison, IL Meridian, MS Bossier City, LA Springfield, MO Texarkana, TX Columbus, MS
Koppers Company, Inc.	Carbondale, IL Denver, CO Florence, SC Gainesville, FL[a] Galesburg, IL Green Spring, WV

TABLE 73. LIST OF CREOSOTE WOOD IMPREGNATION PLANTS IN THE UNITED STATES[151] (Continued)

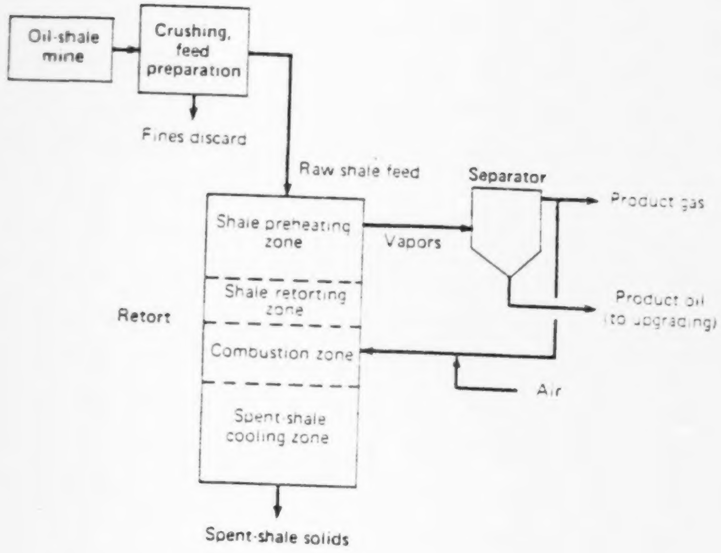
Company	Location
Koppers Company, Inc. (continued)	Grenada, MS
	Guthrie, KY
	Houston, TX
	Kansas City, MO
	Montgomery, AL
	Montgomery, AR
	Montgomery, PA[a]
	Nashua, NH
	North Little Rock, AR
	Oroville, CA
	Orrville, OH
	Port Newark, NJ
	Richmond, VA
	Salem, VA
	Salisbury, MD
	Superior, WI[a]
The Langley Company	Valdosta, GA
Lufkin Creosoting Company, Inc.	Lufkin, TX
Madisonville Creosote Works, Inc.	Madisonville, LA
Manor Timber Company, Inc.	Manor, GA[a]
Marion Pressure Treating Company	Marion, LA
Marshall Wood Preserving Company	Marshall, TX
McArthur Lumber and Post Company, Inc.	McArthur, OH
McCormick and Baxter Creosoting Company	Portland, OR
	Stockton, CA
McCrawie Brothers Wood Preserving Company	Willacoochee, GA
L. D. McFarland Company	Eugene, OR[a]
McFarland Cascade	Olympia, WA
	Tacoma, WA
H. P. McGinley, Inc.	McAlisterville, PA
Mellott Wood Preserving Company	Needmore, PA
W. C. Meredith Company, Inc.	East Point, GA
T. R. Miller Mill Company, Inc.	Brewton, AL
Mississippi Wood Preserving Company	Brookhaven, MS

Retorting temperatures in an internally heated surface retort range from 649 to 704°C (1200 to 1300°F). Due to these relatively high temperatures, product oil from retorting has a lower naphtha content but higher aromatic content than oil generated by externally heated retorts. Retort off-gases, which are diluted by nitrogen from air and carbonate decomposition in the shale, have a Btu value of about 100 Btu/scf.[154]

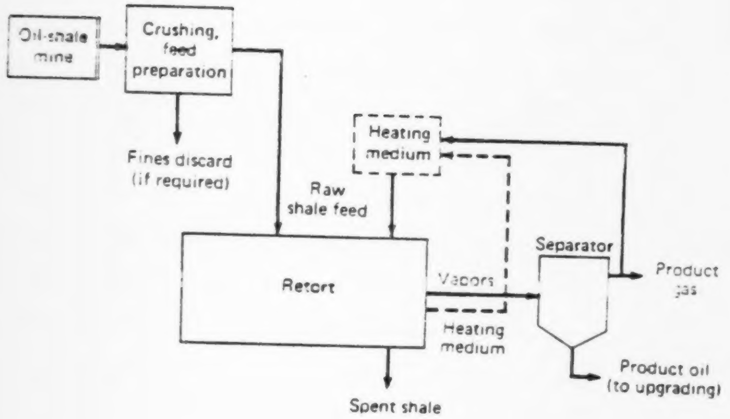
Externally heated surface retorts require a separate heating unit fired by product gas or residual carbon to extract shale oil. Shale is heated either by the hot combustion gases or by means of a heat-carrying medium, typically sand. Retorting temperatures of about 482°C (900°F) are maintained. Because of the lack of outside air injections, off-gases from externally heated surface retorts have a higher heating value (950 Btu/scf) than internally heated surface retorts.[154] Diagrams illustrating both types of surface oil shale retort are given in Figure 37.[154]

In situ oil shale retorting generally falls into one of two categories. True *in situ* processing involves the drilling of injection and production holes from the surface into the oil shale strata to be retorted. These holes are used to fracture the oil shale and create permeability. Once permeability is established, hot fluids or fine fronts are passed from injection wells to production wells where the retorted shale oil is recovered and pumped to the surface.[155]

Modified *in situ* retorting indicates that a portion (15 to 40 percent) of the oil shale is mined and brought to the surface, while the remainder is explosively fractured prior to the ignition of the retort.[155] The retort is then ignited with a propane burner and soon after combustion of the oil shale is self-sustaining. Air and steam are forced into the top of the retort to control the temperature and rate at which the flame front progresses downward through the rubblized layers of oil shale. Temperatures of 871°C (1600°F) are achieved in *in situ* retort systems.[154] As the high temperature flame front proceeds through the oil shale rubble, condensed


Oil-shale mine
Crushing, feed preparation
Fines discard
Raw shale feed
Separator
Product gas
Shale preheating zone
Vapors
Shale retorting zone
Retort
Product oil (to upgrading)
Combustion zone
Air
Spent-shale cooling zone
Spent-shale solids

a. Internally heated retort


Oil-shale mine
Crushing, feed preparation
Fines discard (if required)
Heating medium
Raw shale feed
Separator
Retort
Vapors
Product gas
Heating medium
Product oil (to upgrading)
Spent shale

b. Externally heated retort

Figure 37. Surface oil shale retorting.[154]

shale oil, sour water, and low Btu gas flow downward through the retort into an underground separator room. In this room, shale oil is separated from the water and both liquids are pumped to the surface.[153]

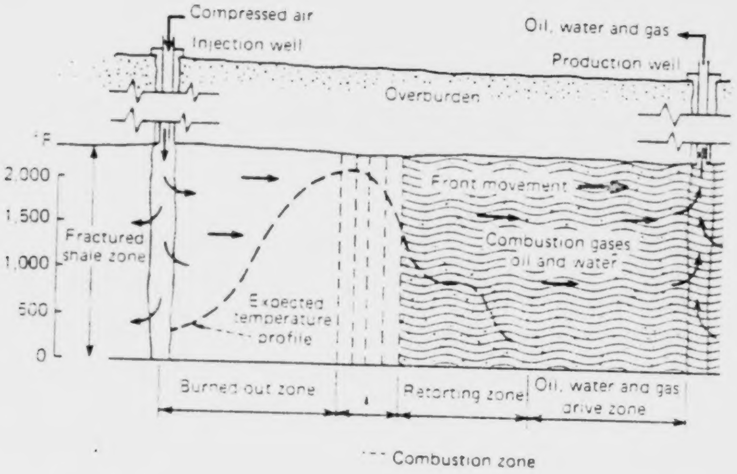
Modified and true in situ oil shale retorting are illustrated in Figure 38.[154]

Off-gases from surface and in situ oil shale retorting, containing POM compounds, steam, inorganic gases, oil droplets, oil vapors, soot, char, unburned oil shale, and spent oil shale, are sent to knockout drums to remove most larger particles in the stream. Following the removal of larger particles, the gas stream is vented to an incinerator to destroy hydrocarbon compounds. Incinerator exhausts, containing sulfur dioxide and particulate matter, are sent to wet scrubbers before final venting to the atmosphere.[153]

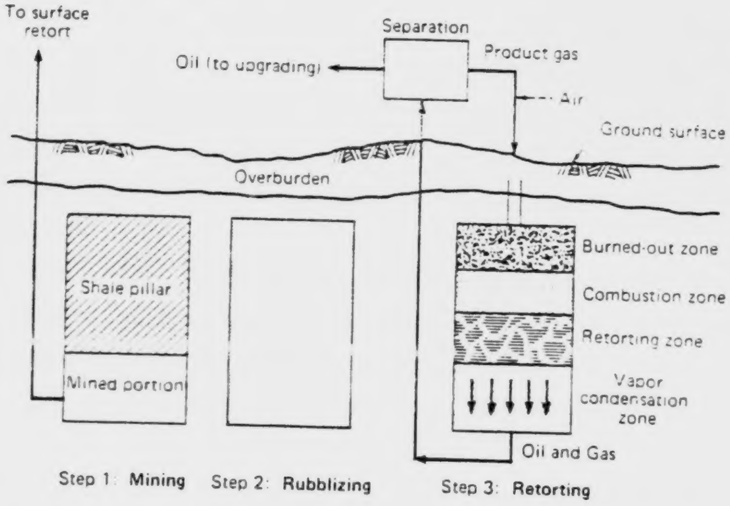
Emission Factors

The amount of information on POM emissions from oil shale retorting is extremely limited. Two sets of data were located that quantified emissions; however, these data were expressed as POM concentrations and not emission factors. In one data set, off-gases from a vertical modified in situ retort were sampled and analyzed in five test runs. Total POM concentrations in retort offgas ranged from 49 to 1207 ug/m^3, with the average being 550 ug/m^3. The average offgas flow rate was 100 m^3/min. The POM quantities measured were the total of materials collected by a glass fiber filter and a Tenax cartridge. The majority of POM compounds measured resided on the glass filter. Specific POM compounds that were identified included anthracene, pyrene, benzo(a)anthracene, and chrysene.[152]

Three of the sampling runs were made three to seven days after initiation of retorting when burn conditions had stabilized. The range of total POM concentrations for these runs was 49 to 206 ug/m^3. The remaining two sampling runs were made three weeks after retorting began. Total POM


Compressed air
Injection well
Oil, water and gas
Production well
Overburden
°F
2,000
1,500
1,000
500
0
Fractured shale zone
Front movement
Combustion gases oil and water
Expected temperature profile
Burned out zone
Retorting zone
Oil, water and gas drive zone
Combustion zone

a. True in situ retorting


To surface retort
Separation
Oil (to upgrading)
Product gas
Air
Ground surface
Overburden
Shale pillar
Mined portion
Burned-out zone
Combustion zone
Retorting zone
Vapor condensation zone
Oil and Gas
Step 1: Mining
Step 2: Rubblizing
Step 3: Retorting

b. Modified in situ retorting

Figure 38. In situ oil shale retorting.[154]

concentrations in off-gases from these runs were 1100 ug/m^3 and 1207 ug/m^3. The authors of Reference 152 speculated that the burning pattern in the retort room may account for the observed increase in total POM over time. As the flame front proceeds down the retort room, increased heating of the shale further down toward the base of the room is occurring, thereby allowing greater mobility of POM compounds into the off-gases.

In a second set of data, total PAH compounds contained in the exhaust gas stream of an incinerator used to control hydrocarbons at a vertical modified _in situ_ retort were analyzed. Total PAH concentrations for two runs were 1142 ug/m^3 and 406 ug/m^3. Of these total PAH quantities measured, only 2 to 10 percent was identified with specific compounds. The specific compounds identified are listed below.[152]

- naphthalene
- acenaphthylene
- acenapthene
- fluorene
- 9,10-dihydroanthracene
- phenanthrene
- anthracene
- 2-methylanthracene
- 9-methylanthracene
- fluoranthene
- pyrene
- benzo(a)anthracene
- chrysene
- benzo(k)fluoranthene
- benzo(b)fluoranthene
- benzo(e)pyrene
- benzo(a)pyrene
- indeno(1,2,3-c,d)pyrene

- dibenzo(a,h)anthracene
- benzo(g,h,i)perylene

In total, over 300 PAH compounds were detected.[152]

The sampling train used to collect these samples consisted of a glass fiber filter followed by an ice bath cold trap followed by two Tenax cartridges in series. Most of the PAH material collected during the test resided in the cold trap of the sampling train.

Source Locations

As of January 1986, no commercial scale oil shale retorting was being performed in the United States. In many cases, retorting projects have ceased operations because Federal funds supporting the projects have been withdrawn.[156] Potential retorting that may be performed in the United States is most likely to occur in either Colorado, Utah, or Wyoming as the bulk of reclaimable oil shale deposits lie in these States. The primary area of activity would lie where these three State boundaries meet in northeastern Utah, northwestern Colorado, and southwestern Wyoming. The map in Figure 39 illustrates the main zones of oil shale deposits in these States and the United States as a whole.[155]

ASPHALT PAVING AND COAL TAR PITCH AND ASPHALT ROOFING OPERATIONS

A moderate amount of information exists in the literature that indicates asphalt paving and roofing and coal tar pitch roofing operations to be potential POM emission sources.[157-159] The principal focus of the work in the literature has been on the health hazards presented to workers by these emissions and not on overall environmental implications. For this reason, the majority of the POM data that exist for these operations is in the form of ambient air and worker area personal sample POM concentrations. Classical emission factors (i.e., mass POM/mass of material used or

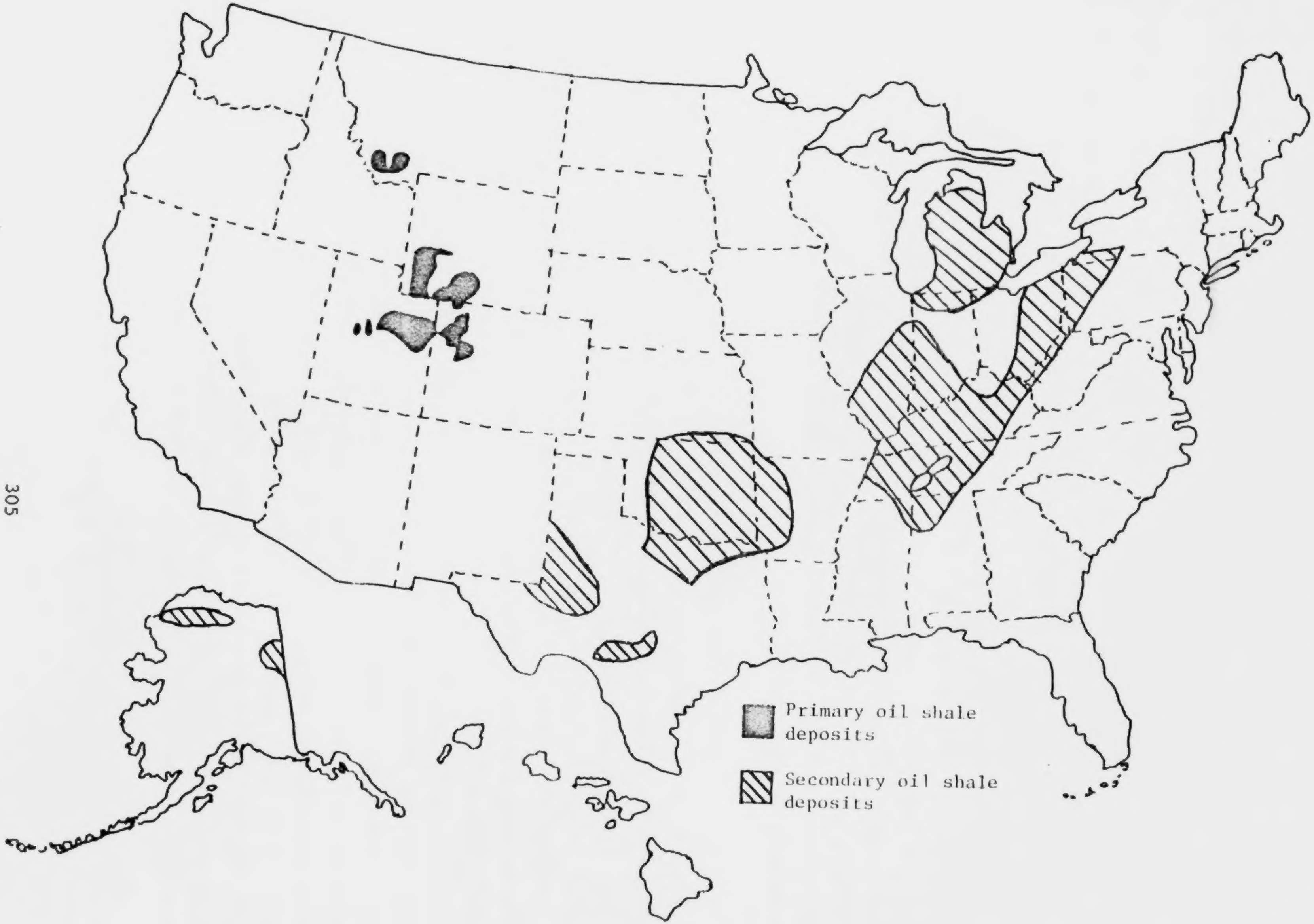

Primary oil shale deposits
Secondary oil shale deposits

Figure 39. Principal areas of oil shale deposits in the United States.[155]

produced) are not available. The data that are available demonstrate that asphalt paving and roofing and coal tar pitch roofing are fugitive POM emission sources.

During asphalt paving operations, POM emissions have been measured (as concentrations) that are associated with pavement preparation, pavement application, and post-application releases. Polycyclic organic matter concentrations have been detected both in the breathing zones of paving workers and in downwind ambient air. The source of the majority of POM compounds measured in connection with asphalt paving operations is the asphalt paving material. At two paving operations tested, the paving raw materials had total POM concentrations of 218 ug/g and 183 ug/g.[157,158] In both of these samples, chrysene and benzo(a)anthracene constituted about 85 percent of the total POM.

Measured concentrations of POM associated with asphalt paving operations are summarized in Table 74.[158] The POM measured was dominated by fluoranthene, benzo(a)anthracene, pyrene, and chrysene. Benzo(a)pyrene levels were very minimal.

Through a series of laboratory experiments, POM emissions were shown to also be released from freshly paved asphalt under differing light and humidity conditions. In the experiments, a freshly paved cell of asphalt was subjected to the equivalent of summer sunlight using a 2500 watt lamp. Potential POM emissions released from the asphalt cell were collected in a XAD-2 resin trap. Collected samples were analyzed by GC/MS and high pressure liquid chromatography (HPLC). Naphthalene, methyl- and ethyl-naphthalene, biphenyl, anthracene, and phenanthracene were routinely observed by GC/MS analysis. The HPLC technique, which is more sensitive to POM, detected anthracene, benzo(a)pyrene, fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, pyrene, fluorene, chrysene, acenophene, benzo(g,h,i)fluoranthene, and indeno(1,2,3-c,d)pyrene.[157]

TABLE 74. POM CONCENTRATIONS MEASURED IN AIR AROUND ASPHALT PAVING OPERATIONS[158]

POM Compound	Paving Site A - POM Concentration, ug/m^3 [a]		Paving Site B - POM Concentration, ug/m^3 [a]	
	Ambient Air Near Site	Paving Operation	Ambient Air Near Site	Paving Operation
Fluoranthene	1.19	0.92	0.48	0.78 - 0.91
Pyrene	0.51	0.51 - 0.85	0.04	0.33 - 2.14
Benzo(a)anthracene	0.23	3.79 - 6.59	0.03	2.25 - 8.78
Chrysene	0.19	0.19 - 2.49	0.10	0.71 - 1.05
7,12-Dimethylbenz(a)anthracene	0.01	0.02 - 0.07	b	0.03 - 0.14
Perylene	0.01	Trace - 0.06	0.01	Trace - 0.01
Benzo(k)fluoranthene	0.01	0.01 - 0.03	0.01	0.01 - 0.05
Benzo(a)pyrene	Trace	0.01 - 0.02	Trace	Trace - 0.01
Benzo(g,h,i)perylene	0.04	0.03 - 0.10	0.03	0.03
Dibenz(a,h)anthracene	0.01	Trace - 0.01	b	0.01
Indeno(1,2,3-c,d)pyrene	0.01	0.03 - 0.04	0.01	0.01
TOTAL	2.21	5.57 - 10.20	0.71	4.32 - 12.99

[a] The sampling and analysis procedures used measured both particulate and vaporous POM.

[b] Data not determined.

The typical concentrations of POM released from paved asphalt exposed to sunlight, as determined by laboratory experiments, are summarized in Table 75.[157] The effect of differing light and humidity conditions on POM and benzo(a)pyrene concentrations from the asphalt are illustrated in Table 76.[157] Under normal light but zero humidity conditions, POM levels are only about 20 to 25 percent of what they were when measured under normal daytime conditions (Table 76). When compared to Table 75 and the results for experiments 1 and 2, experiments 3 and 4 in Table 76 indicate that POM releases from freshly paved asphalt are strongly related to light exposure. An examination of the benzo(a)pyrene data in Table 76 implies that benzo(a)pyrene formation is also strongly related to pavement light exposure.[157]

All experiments conducted to obtain the data in Tables 75 and 76 were performed on a simulation of freshly applied asphalt pavement. No examination was made of potential releases over time.[157]

Similar to asphalt paving, several studies have been conducted to determine the quantity of POM emissions that asphalt and coal tar pitch roofing workers are exposed to. Roofing workers may be exposed to POM compounds during preparation (heating) of the asphalt or coal tar pitch prior to application, during application, and during roof tear-off, which must be performed before a new roof can be applied. New construction roofs would not have a tear-off step.

Generally, for new asphalt and coal tar pitch roofs on existing structures, the tear-off operation begins by sweeping loose gravel from the old roof with a power broom. The existing asphalt or pitch layer is broken up down to the existing level of insulation using a power cutter. Once the breaking process is accomplished, the old roof is pried up and scraped from the surface. After tear-off operations are complete, rigid insulation is applied with hot asphalt and tar paper is applied over the insulation using hot asphalt or coal tar pitch. Other materials such as aluminum and rubber membranes may also be applied to the insulation using hot asphalt or coal tar pitch.[159]

TABLE 75. POM CONCENTRATIONS RELEASED FROM FRESHLY PAVED ASPHALT EXPOSED TO LIGHT[157]

Experiment Number	Test Conditions: Humidity	Test Conditions: Asphalt Temperature	POM Concentration, ng/m^3	Percent POM that is Benzo(a)pyrene
1.	72%	42°C (107°F)	2139	14%
2.	76%	43°C (110°F)	1729	14%
3.	85%	38°C (100°F)	2280	21%
4.	78%	37°C (99°F)	2310	0%

TABLE 76. POM CONCENTRATIONS FROM FRESHLY PAVED ASPHALT UNDER DIFFERING LIGHT AND HUMIDITY CONDITIONS[157]

Experiment Number	Light	Test Conditions		POM Concentration, ng/m^3	Percent POM that is Benzo(a)pyrene
		Humidity	Asphalt Temperature		
1.	On	0%	43°C (110°F)	352	9.9%
2.	On	0%	45°C (113°F)	527	10%
3.	Off	0%	44°C (111°F)	99	Not detected
4.	Off	0%	45°C (113°F)	117	Not detected
5.	Visible light only	71%	38°C (110°F)	13,333	Not detected
6.[a]	On	81%	38°C (100°F)	39.7	Trace

[a] In this experiment pure nitrogen and not air was used to conduct the sampling.

Polycyclic organic matter concentrations that have been measured in and around asphalt and coal tar pitch roofing operations are given in Table 77.[158] Concentrations associated with coal tar pitch operations are significantly greater than those from asphalt roofing because coal tar pitch contains on average 800 times more total POM than asphalt. As would be expected, concentrations are greatest from the asphalt and pitch preparation operations because in this step, the materials are being heated to make them fluid enough for pumping and application. Total POM results for the asphalt roofing sites are fairly consistent with the exception of the preparation source value at site 1, which is about 5 to 7 times greater than preparation source values for the other asphalt sites. The coal tar pitch data are not as consistent overall as the asphalt data; however, they do not exhibit any variability as great as the asphalt preparation source at site 1.

The only emission concentrations information on POM emissions from roof tear-off operations was contained in Reference 159. In this study, POM concentrations resulting from a coal tar pitch tear-off operation were significantly greater than those from an asphalt tear-off operation (i.e., 100 ug/m^3 compared to a trace). Concentrations were also determined for application operations and these were more consistent. For hot coal tar pitch application, source emissions had a total POM concentration of about 30 ug/m^3. The same concentration at a hot asphalt application site was 20 ug/m^3. No other information could be identified to confirm the indication that coal tar pitch tear-off operations are significantly greater POM emitters than either asphalt tear-off operations or asphalt and coal tar pitch application operations.[159]

TRANSFER AND HANDLING OF COAL TAR AND PETROLEUM PITCH

One reference was identified that presented data to indicate that POM emissions are released to the atmosphere during handling and transfer operations involving coal tar and petroleum pitch.[160] In this study, which was conducted by the National Institute for Occupational Safety and Health (NIOSH), an assessment was made of the health hazard presented to workers

TABLE 77. POM CONCENTRATIONS ASSOCIATED WITH ASPHALT AND COAL TAR PITCH ROOFING OPERATIONS[158]

Site Number/ Roofing Type	Sample Source[a]	POM Concentrations, ug/m^{3}[b,c]											
		Fl	Py	B(a)A	Chry	DMBA	Per	B(k)F	B(a)P	B(ghi)Per	DB(ah)A	IP	Total
I/Asphalt	Ambient	0.53	0.10	0.11	0.10	0.01	Trace	0.01	0.01	0.04	ND	ND	0.91
	Application	1.09	1.5	11.7	2.09	0.64	0.05	0.14	0.08	0.32	ND	ND	17.6
	Preparation	10.3	5.3	68.0	26.5	0.26	0.59	0.48	0.43	0.44	0.15	ND	112.45
II/Asphalt	Ambient	0.22	0.21	0.17	0.19	0.04	0.01	0.03	0.01	0.10	ND	ND	0.98
	Application	1.87	0.63	9.32	5.25	0.07	0.03	0.07	0.04	0.02	ND	ND	17.27
	Preparation	1.41	0.46	8.53	3.92	0.05	0.06	0.05	0.04	0.05	ND	ND	14.53
III/Asphalt	Ambient	0.09	0.05	0.14	0.10	Trace	0.02	0.01	Trace	0.03	0.01	ND	0.45
	Application	0.72	0.19	9.63	5.34	0.14	0.09	0.08	0.05	0.11	ND	ND	16.35
	Preparation	1.97	1.25	11.4	5.1	0.05	0.02	0.18	0.08	0.27	0.03	ND	20.35
IV/Coal Tar Pitch	Ambient	0.31	0.35	0.59	0.40	0.07	0.01	0.06	0.01	0.07	0.04	ND	1.93
	Application	97.4	36.7	64.8	26.4	0.81	0.62	0.96	0.40	ND	ND	ND	228.1
	Preparation	144.0	110.0	257.0	798.0	1.37	3.49	2.78	4.22	3.24	0.35	0.98	1325.4
V/Coal Tar Pitch	Ambient	0.33	0.34	1.59	0.79	0.05	0.08	0.08	0.08	0.11	0.04	0.05	3.54
	Application	154.0	162.0	145.0	77.6	1.22	1.93	2.03	1.22	1.48	0.80	0.38	547.7
	Preparation	51.4	188.0	61.9	32.0	0.88	0.83	1.0	0.62	0.28	0.11	0.11	337.1
VI/Coal Tar Pitch	Ambient	0.70	0.28	3.78	0.74	0.02	0.01	Trace	0.02	0.01	ND	Trace	5.59
	Application	53.0	44.8	109.0	28.1	0.28	0.57	0.60	0.93	0.28	ND	0.08	237.4
	Preparation	87.3	87.3	523.0	152.0	16.3	6.97	5.19	11.3	4.16	1.49	1.81	896.8

[a] Ambient samples mean ambient air in the vicinity of roofing operations. Application samples are the personal air samples of workers applying asphalt or coal tar pitch roofing. Preparation samples are the personal air samples of workers preparing hot asphalt or coal tar pitch for application.

[b] The sampling and analysis procedure used measured both particulate and vaporous POM.

[c] The key for the POM compounds is as follows: Fl - Fluoranthene; Py - Pyrene; B(a)A - Benzo(a)anthracene; Chry - Chrysene; DMBA - 7,12-Dimethylbenz(a)anthracene; Per - Perylene; B(k)F - Benzo(k)fluoranthene; B(a)P - Benzo(a)pyrene; B(ghi)Per - Benzo(g,h,i)perylene; DB(ah)A - Dibenz(a,h)anthracene; IP - Indeno(1,2,3-c,d)pyrene

from handling coal tar and petroleum pitch. The.results of the assessment showed that coal tar and petroleum pitch handling and transfer operations are potential sources of fugitive POM air emissions.[160]

In the coal tar pitch operation that was investigated, coal tar pitch was being transferred from a river barge to an ocean barge by means of a crane. In the petroleum pitch operation, pitch was being loaded from railroad cars to an ocean barge. Railroad cars are positioned over a hole in the dock so that when a trap door is opened in the bottom of the rail car, pitch falls out onto a conveyor. The conveyor carries the pitch to a chute at the edge of the dock, where it drops down and onto a barge.[160]

Worker exposure to particulate POM emissions during both of these operations was evaluated by taking personal breathing zone air samples and handling/transfer area air samples. The POM compounds and concentrations that were detected are summarized below.[160]

POM Compound	Concentration (ug/m^3)	Operation Type
Benzo(k)fluoranthene	0.02 - 12.88	Coal Tar Pitch
Benzo(b)fluoranthene	0.05 - 34.76	Coal Tar Pitch
Benzo(a)anthracene	0.11 - 34.76	Coal Tar and Petroleum Pitch
Benzo(e)pyrene	0.09 - 38.85	Coal Tar Pitch
Benzo(a)pyrene	0.11 - 38.85	Coal Tar Pitch
Pyrene	0.46 - 44.99	Coal Tar and Petroleum Pitch
Chrysene	0.32 - 26.58	Coal Tar Pitch
Fluoranthene	0.93 - 3.72	Petroleum Pitch

While it is not possible to quantify potential POM releases from pitch handling and transfer with these data, they do indicate that fugitive POM emissions are occurring.

At the river terminal where the Reference 160 tests were conducted, a coal tar or petroleum pitch transfer operation takes place every 2 to 3 weeks, each lasting about 16 hours. Therefore, as a POM air emissions source, pitch handling and transfer operations would be intermittent and variable. They would most likely be located at river and marine terminals along major water transportation routes that handle industrial commodities (grain, fertilizer) and basic raw materials (mineral ores, coal).

BURNING COAL REFUSE PILES, OUTCROPS, AND MINES

Process Description

Because they are sources of highly inefficient combustion, burning coal refuse piles, outcrops, and mines have been identified as potential POM air emission sources.[161,162]

Coal as it comes from a mine contains various amounts of impurities such as slate, shale, calcite, gypsum, clay, and pyrite. These waste impurities are separated from coal prior to its being marketed. This waste material or coal refuse is commonly piled into banks or stored in impoundments near coal mines and coal preparation plants. Coarse refuse (i.e., greater than 595 um diameter) is deposited into piles by dump trucks, mine cars, conveyors, or aerial trams. Indiscriminate dumping and poor maintenance of refuse piles are two practices that can result in spontaneous combustion of refuse piles.[161]

Fine coal refuse (i.e., material less than 595 um diameter) is often pumped to impoundments or settling ponds as slurry and allowed to settle. Filters and clarifiers may also be used to aggregate the fine refuse. Impoundments are usually constructed of existing coal refuse, as it is the cheapest fill material available. Settled fine refuse is periodically removed from the impoundment and dumped on the larger coal refuse piles. Impoundments may also be sources of spontaneous coal combustion.[161]

Spontaneous ignition and combustion of coal refuse piles and impoundments is mainly an oxidation phenomenon involving coal, associated pyrite, and impure coal substances. The oxidation of carbonaceous and pyrite material in the coal refuse is an exothermic reaction. The temperature of a coal refuse pile or portions of it increases if the amount of circulating air is sufficient to cause oxidation but insufficient to allow for dissipation of the resulting heat. The temperature of the refuse pile then increases until ignition temperature is reached. Experimental evidence has indicated that the heat of wetting of coal is greater than the heat of oxidation of coal; therefore, the presence of moisture in air accelerates the self-heating process in coal refuse piles. For this reason, the relative humidity of ambient air is a key factor affecting coal refuse pile fires.[161]

Coal textural moisture content (i.e., moisture retained in coal pores and void spaces) is also an important variable in the occurrence of coal refuse fires. Upon exposure to air, moisture is lost from the coal pores thereby leaving a significant area for oxygen adsorption. Increased oxygen adsorption facilitates greater oxidation and promotes the development of coal refuse pile fires.[161]

Oxidation of pyrite impurities in coal refuse piles is another supplementary factor which enhances the possibility and severity of coal refuse combustion. Oxidation of pyrite is a highly exothermic reaction that increases the temperature of surrounding oxygen material and thus increases the coal's rate of oxidation.[161]

Other factors contributing to or affecting coal refuse pile combustion are:

- external sources of heat such as steam pipes, sunlight, etc.; and
- coal particle size.

Fine particles pose competing situations. In one case, a predominance of fine particles offers greater total surface area to oxidation, thereby permitting more rapid oxidation. Conversely, smaller particles allow for denser coal packing which can reduce the flow of air through the pile and decrease the rate of oxidation.[161]

Coal refuse piles are considered to be burning if they exhibit either of the following conditions.

- presence of smoke, fume, flames, thermal waves above the pile, or fire glow
- an internal temperature of 93°C (199°F)

The spontaneous combustion of coal in outcrops and abandoned mines is also attributable to oxidation phenomena involving coal, moisture, and pyrite impurities. Other factors affecting combustion in mines and outcrops include coal rank, coal strata geology, and the coal strata temperature profile. Low-rank coals such as subbituminous or high-volatile bituminous are more susceptible to spontaneous combustion than a high-rank coal such as low-volatile bituminous or anthracite. Low-rank coals contain a greater amount of moisture and pyrite impurities than high-rank coals, which enhances their propensity for spontaneous combustion. The presence of faults in coal seams enhances oxidation by providing channels for greater volume and more distributed air flow. Coal strata temperature typically increases with depth. Oxidation rate, therefore, will increase with depth, making the seam more vulnerable to spontaneous combustion.[161]

To summarize, spontaneous combustion and resulting emissions from coal refuse piles, outcrops, and mines are primarily affected by the following factors.

Coal Refuse Piles

- oxygen concentration in the pile which is dependent on pile particle size distribution, type of pile surface, and wind speed

- type of coal
- relative humidity of ambient air
- coal moisture content
- type of refuse
- temperature

Outcrops and Mines

- oxygen concentrations, which are affected by air leakage through natural faults and cracks and air leakage through holes caused by subsidence
- type of coal
- depth of stratum
- relative humidity of ambient air
- coal moisture content
- temperature

Various techniques exist to control emissions from burning coal refuse piles, outcrops, and mines. The majority of these techniques are based on eliminating the fire's oxygen supply to extinguish it and on preventing the fire from spreading. The primary methods that have been applied to refuse piles are described below.[161]

Isolation - The burning area is isolated from the remainder of the refuse pile by trenches and is quenched with water or blanketed with incombustible material.

Blanketing - Some piles are extinguished by leveling the top, then sealing it, and the sides with fine, incombustible material such as fly ash, clay, quarry wastes, or acid mine drainage sludge. Heavy seals of such material are necessary to avoid erosion. The use of clay is limited as it cracks over hot spots impairing the seal.

Grouting - A slurry of water and finely divided incombustible material, such as pulverized limestone, fly ash, coal silt, or sand, is forced into the burning pile so as to provide some cooling action and also to fill the voids to prevent air from entering the pile.

Explosives - Many burning piles have an impenetrable, ceramic-like, clinker material surface which does not allow the penetration of slurries and water. In this case, explosive charges are placed deep into the bank through horizontally drilled holes. The explosion creates fissures in the fused covering material. Water is then applied through these crevices and the quenched material is loaded out.

Spraying - In this method, water is sprayed over the entire refuse bank. However, this is only a temporary solution as the pile reignites and burns, often with renewed vigor, once the water spray is stopped.

Accelerated Combustion and Quenching - The burning refuse material is lifted by a dragline and dropped through air into a water-filled lagoon 15 to 30 m (49 to 98 ft) below for the purpose of burning off the combustible material completely during the drop. Another dragline and bulldozers are used to remove the quenched material from the lagoon floor and compact it into a tight, dense fill material.

Ponding - Retaining walls are constructed around the perimeter of a refuse bank after subdividing the surface into a series of level discrete areas and each area is filled with water to flood the fire. This method has not proven to be successful because flooding with water may cause explosions due to the formation of water gas and water penetration into the pile is poor.

Cooling and Dilution - Water is sprayed on the burning pile from multiple nozzles and the cooled refuse is mixed, by bulldozer, in a one-to-one volume proportion with soil and/or burned out refuse from a nearby area. The mixture is then compacted by heavy equipment.

Hydraulic Jets - High velocity water connons are used to quench the burning refuse material. The quenched material is then relayered and compacted by a dragline and bulldozer.

With fires in coal outcrops or abandoned mines, the principle of control is to isolate the burning material and prevent air from reaching it. The techniques used for this purpose are described below.[161]

Loading Out - This method involves digging out the burning and heated material, then cooling it with water or spreading it on the ground. This method is effective if the fire is of recent origin or mild enough to be accessible.

Fire Barriers - A barrier of incombustible material is used to confine and isolate the fire from the main body of coal. The isolated area is also surface sealed to extinguish the fire. The barrier can be an open trench, between the fire area and the threatened area, which is backfilled with incombustible material such as earth, fly ash, or granulated slag. A plug barrier is used if the overburden is excessive, since it is impractical to excavate a trench from outcrop to outcrop around an abandoned mine fire. A plug barrier starts at the outcrop and terminates when the overburden depth exceeds 20 m (66 ft). The plug barrier is always used in conjunction with a surface seal. A surface seal on the fire side of the plug has been observed to be effective in controlling abandoned mine fires if the overburden is in excess of about 20 m (66 ft).

Flushing - In this method, the void spaces around an underground fire are filled with water or an incombustible material such as fly ash. The incombustible material can be applied pneumatically or as a slurry.

Surface Sealing - This technique involves closing the surface openings surrounding the fire site to prevent ventilation of the fire. The surface seal is established by plowing the surface to a depth of several meters with an angle dozer to create a blanket of pulverized earth that effectively seals the surface.

Emission Factors

One emission factor was found in the literature relating to POM emissions from burning coal refuse piles, outcrops, or mines.[161] Particulate POM emissions from a burning coal refuse pile have measured been measured by using a high-volume filter air sampling device. The total POM emission factor for burning coal refuse piles developed from these test results is 0.019 mg/hr-m^3 of burning coal refuse.[161] Assuming an average coal refuse pile density of 1.5 Mg/m^3 (0.05 ton/ft^3), an equivalent POM emission factor of 0.013 mg/hr-Mg of refuse burned can be calculated. The POM compounds identified in the collected refuse pile emissions are listed below.

- dibenzothiophene
- anthracene/phenanthrene
- methylanthracenes/phenanthrenes
- 9-methylanthracene
- fluoranthene
- pyrene
- benzo(c)phenanthrene
- chrysene/benz(a)anthracene
- dimethylbenzanthracenes
- benzo(k)fluoranthene
- benzo(b)fluoranthene
- benzo(a)pyrene/benzo(e)pyrene/perylene
- 3-methylcholanthrene
- dibenzo(a,h)pyrene
- dibenzo(a,i)pyrene
- dibenz(a,h)anthracene
- dibenz(a,c)anthracene
- indeno(1,2,3-c,d)pyrene
- 7H-dibenzo(c,g)carbazole

Source Locations

Burning or potentially-burning coal refuse piles, outcrops, and mines are linked to coal mining and coal preparation plant locations. No recent information on the sources of burning refuse piles, abandoned mines, and outcrops could be identified from the Bureau of Mines or the Office of Surface Mining. Data for 1972 indicate that West Virginia, Pennsylvania, Virginia, and Kentucky accounted for 84 percent of all burning refuse piles and West Virginia and Pennsylvania accounted for 87 percent of the burning refuse impoundments. Given that these States are still major coal mining areas, their status as leading sources of burning refuse sites is probably still valid.[161]

In January 1976, there were 441 fires in abandoned coal mines and outcrops. These fires occurred in 18 coal producing States, with Montana, Wyoming, Colorado, and New Mexico accounting for 66 percent of the fires.

A list of States containing burning coal refuse piles, outcrops, or abandoned mines is presented in Table 78.[161]

PRESCRIBED BURNING AND UNCONTROLLED FOREST FIRES

Process Description

Prescribed burning is defined as the application and confinement of fire in forest and range management under specified conditions of weather, fuel moisture, and soil moisture that will accomplish planned benefits such as fire hazard reduction, control of understory species, seedbed and site preparation, grazing enhancement, wildlife habitat improvement, and forest tree disease control. It differs from uncontrolled forest fires in that it is used only under controlled conditions and is managed so that beneficial effects outweigh costs and possible detrimental impacts. Uncontrolled forest fires refers to fires that are started naturally (lightening), accidentally, or intentionally in forests that burn and spread in generally unpredictable patterns. Prescribed burning and uncontrolled forest fires are both potential sources of POM emissions because combustion in these environments is inefficient and incomplete due to the high moisture content and varying composition of the materials burned.[162-164]

The firing techniques employed in prescribed burning depend on the kind of area to be burned and on local burning conditions. The predominant burning techniques are backing fire, heading fire, ring fire, and

TABLE 78. BURNING COAL REFUSE PILES, IMPOUNDMENTS, ABANDONED MINES, AND OUTCROPS IN THE UNITED STATES BY STATE[161]

State	Refuse Piles[a]		Impoundments[a]		Abandoned Mines and Outcrops[c]
	Active	Inactive[b]	Active	Inactive[b]	
Alabama	7	1	4	12	---[d]
Alaska	1	4	1	---	7
Arizona	---	---	---	---	30
Arkansas	1	---	---	---	---
Colorado	8	37	---	---	66
Illinois	0	9	0	2	---
Indiana	0	6	---	---	---
Kentucky	28	90	1	94	6
Maryland	1	---	---	---	2
Montana	2	12	---	---	105
New Mexico	4	16	---	---	39
North Dakota	0	9	---	---	18
Ohio	7	2	0	3	7
Oklahoma	---	---	---	---	1
Oregon	0	1	---	---	---
Pennsylvania	37	123	16	43	37
South Dakota	---	---	---	---	3
Tennessee	1	3	0	4	---
Texas	---	---	---	---	1
Utah	0	7	0	2	28
Virginia	30	76	2	20	1
Washington	0	4	0	1	2
West Virginia	79	48	41	42	8
Wyoming	0	19	0	2	80
TOTAL	206	467	65	225	441

---

[a] 1972 data.

[b] Indicates not presently burning but could burn.

[c] 1975 data.

[d] Dash indicates that data were not reported by a State.

area-ignition. Often, combinations of these techniques are used at a single burning site. A fifth method of burning known as pile and windrow fires also exists but is not used frequently.[163]

Backing fires are ignited on the downwind side of an area and permitted to spread against the wind. The advance of the active burning zone is slow and most of the fuel is consumed within this zone. In this way, smoldering time for the fuel is reduced, and total combustion efficiency of the fire is increased. The backing fire produces the least fire intensity of all techniques, having slow spread rates, a narrow burning zone, and short flames. It therefore lends itself to use in heavy fuel accumulations and in removing understory growth and debris where an overstory of crop trees exists.[163]

Heading fires are ignited on the upwind side of an area and spread with the wind. The active burning zone moves rapidly from fuel element to fuel element. Under these conditions, many fuel elements are not consumed completely in the active burning zone. A rather large zone of smoldering fuel is left behind, producing large quantities of products of incomplete combustion. This technique is employed in lighter fuels if the amount of heat produced will not scorch overstory tree crowns. Heading fires are also preferred for control of brownspot disease in longleaf pine.[163]

Ring firing is accomplished by igniting the perimeter of the intended burn area and allowing the fire to burn towards the center. This technique results in a rapid, relatively hot fire and finds particular application in reducing timber-harvesting residues in clearcut areas.[163]

Area-ignited fires are set by igniting the intended burn area in many individual spots and allowing individual fires to burn in all directions as they come together. This type of fire is frequently employed in clearcut areas when a rapidly-developed and high-rising convection column is desired. It will have high variability in burning intensity as junction zones of increased intensity form.[163]

Pile and windrow fires are used in management programs to effect more complete consumption of large pieces of material, such as logging residue. When hand-piling is practiced, the objective is to dispose of only the fine fuels and the smaller diameter branchwood. The preferred firing technique calls for igniting the finer fuels around pile perimeters to obtain rapid heat buildup, permitting the larger fuel elements to become ignited and consumed. The extreme fire intensity may adversely affect the soil immediately beneath piles. In poorly conducted operations, piles and windrows may contain large amounts of soil when machine piled. This may result in areas which burn and smolder for days.[163]

In addition to firing techniques, emissions from prescribed burning and uncontrolled forest fires are affected primarily by environmental factors and fuel conditions. The most prominent environmental factors influencing emissions are wind speed and direction, rainfall history, and relative humidity. Secondary environmental factors include degree of cloud cover, air temperature, atmospheric stability, and degree of land slope. Wind speed, wind direction, and, to a lesser extent, slope of land all determine how fast a heading fire or a backing fire will spread. Generally, a faster moving fire front burns less efficiently, producing more smoldering and greater emissions.[163]

The most important fuel characteristics affecting emissions from burning are fuel moisture content and fuel loading (i.e., amount of fuel per unit area). Fuel arrangement and fuel species composition (i.e., fuel type, fuel age, and fuel size) are also key variables affecting emissions. High moisture content reduces combustion efficiency, which in turn produces greater emissions. Fuel loading level is directly related to emissions, the more fuel burned, the greater the emissions. Fuel arrangement can affect burn intensity and completeness by affecting air supply and it may influence the fire spreading pattern. Fuel composition affects emissions in several ways. Different fuels (wood, grass, brush, leaves) have varying compositions, which upon combustion, produce different qualities and quantities of emissions. Fuels of differing ages contain varying moisture contents (seasoned versus green fuels) and varying organic constituents which may affect overall burning emissions. Emissions may also be affected if fuel composition has been modified by organic forest treatment chemicals such as pesticides, herbicides, etc.[163,165]

As applied to prescribed burning, the term control technology may be defined as either alternatives to burning in which prescribed fires are no longer used, or the use of control techniques in which emissions are reduced, dispersed, or directed away from population areas. Alternatives to prescribed burning include mechanical and chemical treatment of forest areas, improved forest utilization, and no forest treatment of any type. The feasibility of using an alternative approach varies with the needs and conditions of the particular forest site.

Different types of mechanical treatment can be used to clear away brush and trees, to prepare land for planting, to break up slash into finer material, and to dispose of slash or brush by burial in gentle terrain. These techniques are not effective for control of understory species without damage to the overstory, for disease control, for reduction of fire hazard (except burial), or for wildlife habitat improvement. Mechanical choppers and shredders can be used to clear away brush and trees for tree planting in open areas. The debris left behind by these kinds of equipment may have to be disposed of to avoid a fire hazard. In addition to choppers and shredders, bulldozers or tractors may be used to clear land for planting and to bury slash material (logging waste). However, this kind of clearing has the potential for soil compaction and increased erosion.[163]

Chemical treatments, such as the application of herbicides, have been used for seedbed preparation and brush control purposes. The development of selective herbicides (compounds that are only toxic to certain species) has made this technique useful in more applications. Such treatments, however, can only be applied to live vegetation and do nothing to reduce fire hazard. Potentially, the risk of fire may actually increase as the dead vegetation dries. Recent bannings on the use of once major herbicides, such as 2,4,5-T, have greatly limited the use of chemical treatment as an alternative to prescribed burning.[163]

Improved utilization is an attractive alternative to prescribed burning that encompasses both improved harvesting techniques that generate less slash material and new end uses for material that is normally burned. Examples of improved harvesting methods that are being used or under development include:

- directional felling to reduce log breakage,
- prelogging or postlogging to recover small diameter timber,
- better handling techniques that will accept material normally discarded as slash, and
- design of contractual agreements to encourage recovery of small size material.

The elimination of any form of treatment including prescribed burning poses no immediate adverse effects to the environment, but it does not accomplish any of the benefits for which prescribed fires are used. Moreover, no treatment for extended periods of time can lead to increased risks of losses due to wildfire, insect infestation, and diminished species diversity and site productivity. The no treatment option cannot be considered a viable alternative in most situations.

When prescribed burning is used, emissions control and/or emissions impact reduction can be effected by utilizing low emission fuel conditions, firing techniques, and meteorological conditions. Fuel conditions can be optimized and overall emissions reduced by:

- regulating the time between burns to control fuel loading,
- burning at lower fuel moisture contents, and
- modifying fuel arrangement to facilitate better air flow and more intense and complete combustion.

The ability to reduce emissions by altering the firing technique is limited because firing techniques are dictated by the type of fuel to be burned and the objectives of the prescribed burning. However, field and laboratory tests have indicated that different firing techniques do have varying levels of emissions. For example, backing fires emit less particulate matter than heading fires.[163]

Utilizing meteorological conditions to minimize the impact of prescribed burning emissions involves burning when conditions are best for directing emission plumes away from receptor areas and for obtaining maximum atmospheric diffusion of the plume. The key factors to examine in determining the optimal emissions dispersion period or situation are mixing height, atmospheric stability, wind speed, and wind direction. Emissions dispersal is optimal when the atmosphere is unstable and the mixing height is high above the earth's surface.[163]

A special stability situation occurs when there is an inversion layer in which the air temperature increases with height. An inversion layer acts as a lid that tends to trap rising emissions near ground level. Consequently, prescribed burning is often precluded when an inversion layer is present. Conversely, inversions lower in elevation than the area where prescribed burning is being done tend to limit emissions below the inversion height. In this way, valleys are often buffered from emissions due to burning at high mountain elevations.[163]

Currently, the use of meteorological scheduling to specify times for prescribed burning, for the purpose of reducing emission impacts, is prevalent.

Emission Factors

No POM emission factor data exist that are based on tests of actual prescribed burning or uncontrolled forest fires. However, emission factor data have been developed by the United States Forest Service by simulating forest burning conditions in a laboratory. In these tests, various loadings of pine needles were burned on a metal table equipped to change slope to simulate wind effects. All emissions from burning were channeled through a large stack where particulate matter was collected by a glass fiber filter in a modified high-volume sampler. Collected samples were analyzed for POM compounds by GC/MS. The results of these tests are given in Tables 79, 80, and 81.[165]

In Table 79, individual POM species and total POM emission factors measured for backing and heading fires are presented. These data indicate that backing fires would generate considerably greater POM emissions than heading fires. With heading fires, the highest emissions were produced by the maximum fuel loading case (2.4 kg/m^2). Somewhat unexpectedly, the highest emissions from backing fires occurred with the minimum fuel loading case (0.5 kg/m^2).[165]

As shown in Table 79, the predominant POM compounds found in backing fire emissions are generally different from those found in heading fire emissions. In backing fire emissions, chrysene/benz(a)anthracene, pyrene, and methyl pyrene/fluoranthene are predominant. Benzo(a)pyrene constitutes on average about 2 percent of total POM. In heading fire emissions, anthracene/phenanthrene, methyl anthracene, methyl pyrene/fluoranthene, and pyrene are the most prevalent compounds.[165] Benzo(a)pyrene constitutes on average only about 0.4 percent of heading fire total POM emissions.

The difference in POM emissions during the flaming and smoldering phases of a fire are illustrated in Table 80. The smoldering phase would be expected to produce greater POM emissions because combustion processes during smoldering are very inefficient. The data in Table 80 confirm this expectation.[165]

Polycyclic organic matter and benzo(a)pyrene emissions, as a function of total suspended particulate emissions from burning pine needles, are given in Table 81 for backing and heading fires.[165]

TABLE 79. PARTICULATE POM EMISSION FACTORS FROM BURNING PINE NEEDLES BY FIRE TYPE[165]

POM Compound	Fire Type and Fuel Loading[a,b]					
	Backing Fires			Heading Fires		
	0.5 kg/m^2	1.5 kg/m^2	2.4 kg/m^2	0.5 kg/m^2	1.5 kg/m^2	2.4 kg/m^2
Anthracene/phenanthrene	12,181	2,189	584	2,525	5,242	6,768
Methyl anthracene	9,400	1,147	449	1,057	4,965	7,611
Fluoranthene	14,563	2,140	687	733	974	1,051
Pyrene	20,407	3,102	1,084	1,121	979	1,133
Methyl pyrene/fluoranthene	18,580	2,466	1,229	730	1,648	2,453
Benzo(c)phenanthrene	8,845	1,808	468	244	142	175
Chrysene/benz(a)anthracene	28,724	5,228	2,033	581	543	836
Methylchrysene	17,753	1,891	877	282	1,287	1,559
Benzofluoranthenes	12,835	1,216	818	164	129	241
Benzo(a)pyrene	3,454	555	238	40	97	33
Benzo(e)pyrene	5,836	1,172	680	61	78	152
Perylene	2,128	198	134	33	24	46
Methylbenzopyrenes	6,582	963	384	65	198	665
Indeno(1,2,3-c,d)pyrene	4,282	655	169	---	---	---
Benzo(g,h,i)perylene	6,181	1,009	419	---	---	---
TOTAL POM	171,750	25,715	10,249	7,632	16,549	22,787

[a] Emission factor units are ug/kg of fuel burned. Results represent the average of duplicate sampling runs.

[b] Fuel moisture content varied between 18 and 27 percent.

TABLE 80. PARTICULATE POM EMISSION FACTORS FROM BURNING PINE NEEDLES BY FIRE PHASES - HEADING FIRE[165]

POM Compound	Heading Fires by Type					
	0.5 kg/m^2		1.5 kg/m^2		2.4 kg/m^2	
	Flaming	Smoldering	Flaming	Smoldering	Flaming	Smoldering
Anthracene/phenanthrene	1,621	7,049	865	9,046	2,351	8,791
Methyl anthracene	539	3,872	667	8,193	1,909	11,447
Fluoranthene	445	2,317	244	1,516	622	1,331
Pyrene	750	3,078	342	1,454	888	1,291
Methyl pyrene/fluoranthene	455	2,383	494	2,501	1,036	3,396
Benzo(c)phenanthrene	228	397	77	189	179	173
Chrysene/benz(a)anthracene	472	1,324	230	769	628	980
Methylchrysene	263	497	343	1,989	466	2,290
Benzofluoranthenes	178	199	69	174	90	347
Benzo(a)pyrene	33	100	17	55	36	140
Benzo(e)pyrene	56	133	45	102	82	203
Perylene	38	33	14	32	27	61
Methylbenzopyrenes	19	397	52	304	75	1,069
Indeno(1,2,3-c,d)pyrene	---	---	---	---	---	---
Benzo(g,h,i)perylene	---	---	---	---	---	---
TOTAL POM	5,097	21,779	3,456	26,324	8,389	31,519

TABLE 81. TOTAL POM AND BENZO(A)PYRENE EMISSION FACTORS FROM BURNING PINE NEEDLES AS A FUNCTION OF TOTAL SUSPENDED PARTICULATE MATTER EMISSIONS[165]

Fire Type	Fuel Loading kg/m^2 (lb/ft^2)	Total POM Emission Factor[a,b]	Benzo(a)pyrene Emission Factor[a,b]
Backing	0.5 (0.1)	13,982	274
Backing	1.5 (0.3)	6,254	135
Backing	2.4 (0.5)	4,084	98
Heading	0.5 (0.1)	873	3
Heading	1.5 (0.3)	399	2
Heading	2.4 (0.5)	392	2

[a] Units of the emission factors are ug of POM or benzo(a)pyrene per g of total suspended particulate matter emitted.

[b] Emission factors represent only particulate matter POM and benzo(a)pyrene.

Source Locations

Information provided by the U. S. Forest Service indicates that the majority of prescribed burning in the United States occurs in the southern/southeastern part of the country.[166] As shown in Table 82, almost 60 percent of national prescribed burning in 1984 was performed in the southern/southeastern region (Forest Service Region 8). The second most prevalent source of prescribed burning in 1984 was the Pacific Northwest which constituted almost 20 percent of the total. California was next in importance of prescribed burning in 1984 with 10 percent of the national total.

The locations of uncontrolled forest fires are not as definable as prescribed burning sites, but the historical record of fires and a knowledge of the locations of primary forest resources can be used to estimate where the majority of forest fires are likely to occur. The southern region and the western part of the country (including California, the Pacific Northwest, and western mountain States) appear to represent the greatest potential for POM emissions from forest wildfires.[164] Forest Service data for 1983 indicate that the southern/southeastern region of the United States constituted 67 percent of the total number of acres burned by wildfires nationally. The western regions of the country contained 17 percent of the wildfire burned acreage. The northern region (Idaho, Montana, North Dakota) of the country contained another 6 percent of acreage destroyed by wildfires.[167]

AGRICULTURAL BURNING

Process Description

Agricultural burning involves the purposeful combustion of field crop, row crop, and fruit and nut crop residues to achieve one or a combination of desired objectives. The typical objectives of agricultural burning are as follows.[162,168]

TABLE 82. DISTRIBUTION OF PRESCRIBED BURNING IN THE UNITED STATES IN 1984[a,166]

Forest Service Region[b]	States Included	Total Acres Burned
1	Idaho Montana	35,132
2	Colorado Nebraska North Dakota South Dakota Wyoming	19,149
3	Arizona New Mexico	34,860
4	Nevada Utah	28,624
5	California	91,313
6	Washington Oregon	159,006
8	Alabama Arkansas Florida Georgia Kentucky Louisiana Mississippi North Carolina Oklahoma South Carolina Tennessee Texas Virginia	525,782
9	All others not in 1-8 or 10	10,039
10	Alaska	1,123
TOTAL		905,028

[a] 1984 in this case means fiscal 1984.

[b] There is no Forest Service Region 7.

- removal and disposal of agricultural residue at a low cost
- preparation of farmlands for cultivation
- cleaning of vines and leaves from fields to facilitate harvest operations
- disease control
- direct weed control by incinerating weed plants and weed seeds
- indirect weed control by providing clean soil surface for soil-active herbicides
- selective destruction of mites, insects, and rodents

The types of agricultural waste subject to burning include residues such as rice straw and stubble, barley straw and stubble, wheat residues, orchard prunings and natural attrition losses, grass straw and stubble, potato and peanut vines, tobacco stalks, soybean residues, hay residues, sugarcane leaves and tops, and farmland grass and weeds.

Polycyclic organic matter are created and emitted during agricultural burning because mixing between the fuel (agricultural residue) and ambient air is poor and because combustion gases from burning are effectively quenched by surrounding ambient air. Poor mixing creates pyrolytic (oxygen deficient) combustion conditions leading to lower temperatures, less efficient combustion, and POM formation and release. Rapid quenching of combustion gases by the huge volumes of air surrounding agricultural burning enhances incomplete combustion, thereby permitting the increased release of unburned hydrocarbons like POM. Polycyclic organic matter may be released from agricultural burning in gaseous form or as a liquid aerosol condensed on solid particulate matter.[162,168]

Potential POM emissions from agricultural burning are related to factors affecting waste combustion efficiency. Waste combustion efficiency is influenced by environmental variables, fuel conditions, and the type of burning or fire management techniques used. Environmental variables affecting combustion efficiency and resultant POM emissions include air temperature, soil moisture, relative and/or absolute humidity, and wind speed and direction. Of the environmental variables, wind speed is the most important factor affecting potential POM emissions. Conditions of the fuel (waste) potentially affecting POM emissions during burning are moisture content, fuel composition, and fuel density. Higher moisture contents and greater fuel densities generally correlate to increased POM emissions because either or both of these conditions tend to reduce overall combustion efficiency. The key fire management techniques influencing POM emissions from agricultural burning are the type of burning used, backing fire or heading fire, and the fuel loading level (i.e., the amount of waste burned in a defined area).

The ability to reduce POM emissions from agricultural burning is primarily related to altering combustion conditions to optimize combustion efficiency. Reducing fuel moisture content has been shown to markedly reduce overall emissions from agricultural burning. A similar trend would be expected for POM emissions because combustion temperatures would be higher with dryer fuel and combustion would be more intense. Evenly distributing wastes prior to combustion would aid drying activities and facilitate more thorough combustion. Waste moisture content is predominantly influenced by environmental conditions. Although not directly controllable, environmental conditions can be optimized in terms of their positive effects on reducing waste moisture content. Lower humidity, higher air temperatures, and higher wind speeds would tend to reduce waste moisture levels.

The use of backfiring (fire progresses in a direction opposite to that of the wind) instead of headfiring (fire progresses in the same direction as the wind) techniques for agricultural burning has been shown to significantly reduce overall particulate emissions. Because backfiring creates a longer waste residence time in the combustion zone, combustion should be more complete and potential POM emissions less.[168]

The most effective means to control POM emissions from agricultural burning is to find alternatives to combustion as a means for accomplishing field sanitation, residue removal, and residue disposal. The most common method of disposing of crop residues is to incorporate the material back into the soil by tilling. This technique only accomplishes residue disposal. Field sanitation is not addressed; however, it may not be an objective in all cases. Mechanical removal of residues is a possible option to burning; however, it is generally expensive, it does not address field sanitation, and the problem of waste disposal still exists once all wastes have been collected. If agricultural burning is only being performed for field sanitation purposes, chemical applications may be a suitable alternative to burning. The effects on the environment of applying herbicides, fungicides, and pesticides to areas for weed, disease, and pest control would have to be weighed against the potential air emissions from burning.[168]

As with other types of open burning, meteorological scheduling can be used to lessen the impact to receptor areas from agricultural burning emissions. Utilizing meteorological conditions to minimize the impact of agricultural burning emissions involves burning when conditions are best for directing plumes away from receptor areas and for obtaining maximum atmospheric diffusion of the plume. The key meteorological factors acting to potentially bring about these conditions are atmospheric mixing height, atmospheric stability, wind speed, and wind direction. Generally, optimal conditions for burning would be the existence of an unstable atmosphere and a high atmospheric mixing height.

Emission Factors

Few POM emission factors exist for agricultural burning. The factors that are available pertain only to benzo(a)pyrene. Burning of whole sugar cane residue was found to produce a particulate benzo(a)pyrene emission factor of 0.00027 kg/Mg (0.00053 lb/ton) of waste burned. Particulate benzo(a)pyrene emissions from burning sugar cane leaf trash were found to be 0.00021 kg/Mg (0.00042 lb/ton) of waste burned.[168]

Additional POM emission factors that may be applied to certain types of agricultural burning are provided in the discussion in Section 4 on Miscellaneous Open Burning.

Source Locations

Agricultural burning is directly correlated with States having a significant agriculture industry. Major agricultural States comprising the majority of agricultural burning include California, Louisiana, Florida, Hawaii, North Carolina, Mississippi, and Kansas.[162]

MISCELLANEOUS OPEN BURNING

The miscellaneous category includes any and all open burning activities not covered in the discussions on coal refuse banks, prescribed burning, forest fires, and agricultural burning. The most readily identifiable types of open burning in the miscellaneous category are municipal refuse open burning; open burning of automobile tires, bodies, and components; open burning of waste railroad ties; and burning of landscaping refuse (grass clippings, leaves, and branches). The purpose of burning in most of these cases is volume reduction to facilitate easier final disposal of the waste material.[169] In the case of automobile body burning, burning is performed to expedite the recovery and recycling of usable metal in the automobiles by removing all organic materials (plastic, vinyl, etc.).[170]

The procedure of open burning in any of the miscellaneous categories is relatively simple. The material to be burned (domestic trash, leaves, etc.) is collected and aggregated in an open space fully exposed to the atmosphere. The materials are ignited and allowed to burn and smolder until all combustible material is consumed or the desired degree of volume reduction is achieved. Combustion efficiency in such operations is typically poor. Potential POM emissions from such operations are highly variable because waste moisture content and combustion conditions (air flow, oxygen levels, waste configuration, degree of exposed surface area) are quite variable from site to site and within the same site. In addition, some wastes may contain organic constituents that are precursors to POM compounds or that accelerate POM compound formation.

Generally, there are two means to control POM emissions from miscellaneous open burning--enclosure of the burning with exhaust ventilation to standard control devices and prohibition of open burning. In most areas of the United Sates, open burning of municipal refuse, automobiles, and grass, leaves, etc., has been greatly restricted, and in the case of municipal refuse and automobiles, completely prohibited. Open burning of grass and leaves has been controlled by requiring collection agencies and the general public to have permits for burning.

The available emission factor data for open burning of municipal refuse automobiles, and landscaping refuse are presented in Tables 83, 84, and 85.[82] The data in Table 83 represent measured POM emission factors from two sets of open burning tests. One set of data was measured in the smoke plumes during outside open burning of municipal refuse, automobile tires, automobile bodies, and landscaping refuse. A second set of data was measured in a laboratory research facility designed to simulate and characterize open burning emissions. The laboratory experiments also burned automobile components, municipal refuse, and landscaping refuse.[82]

In Table 84, the results of the laboratory open burning tests are presented as a function of the amount of waste burned as opposed to being a function of total particulate matter emissions as in Table 83. The factors in Table 84 could be determined for the laboratory open burning tests because all conditions of the tests such as emission rates, flow rates, waste throughput, etc., could be controlled; whereas, conditions could not be duplicated or controlled outdoors.

TABLE 83. POM EMISSION FACTORS FOR OPEN BURNING AS A FUNCTION OF TOTAL PARTICULATE MATTER EMISSIONS[82]

Type of Open Burning	Sampling Point[b]	All Factors in Terms of ug/g of Particulate Collected[a]										
		BaP	P	BeP	Per	BghiP	Anth	Cor	A	Phen	Fl	Total POM
Municipal Refuse	Smoke Plume	11	29	4.5	ND[c]	ND	ND	ND	4.7	ND	13	62.2
Automobile Tires	Smoke Plume	1100	1300	450	72	660	53	81	110	450	470	4746
Landscaping Refuse	Smoke Plume	35	120	21	ND	5.4	ND	ND	4.7	ND	110	296.1
Automobile Bodies	Smoke Plume	270	670	120	33	150	12	15	220	160	450	2100
Municipal Refuse	Lab Stack	28	146	19	ND	12	ND	ND	ND	ND	133	338
Landscaping Refuse	Lab Stack	29	152	14	2.8	12	1.8	ND	ND	ND	100	311.6
Automobile Components	Lab Stack	380	1000	190	35	260	29	32	43	280	710	2959

[a] These ten POM compounds were specifically analyzed for during these tests. Conceivably others existed in the streams that were not identified. The POM compound abbreviations are keyed as follows: BaP - benzo(a)pyrene; P - pyrene; BeP - benzo(e)pyrene; Per - perylene; BghiP - benzo(g,h,i)perylene; Anth - anthanthrene; Cor - coronene; A - anthracene; Phen - phenanthrene; Fl - fluoranthene.

[b] Smoke plume designates that POM measurements were made by placing a high-volume sampler in the smoke plume of an actual outdoors open burning fire. Only particulate matter POM were collected in the smoke plume tests. Lab stack designates that POM measurements were made in a research laboratory designed to simulate open burning. Emissions from simulated open burning were collected by hooding and channeled through a stack for measurement. The sampling procedure in the lab stack tests was designed to collect both particulate and gaseous POM.

[c] ND designates that the compound was not detected.

TABLE 84. POM EMISSION FACTORS FOR OPEN BURNING AS A FUNCTION OF THE AMOUNT OF WASTE BURNED[82]

Type of Open Burning	Sampling Point[b]	All Factors in Terms of ug/lb of Refuse Burned[a]										
		BaP	P	BeP	Per	BghiP	Anth	Cor	A	Phen	Fl	Total POM
Municipal Refuse	Lab Stack	153	800	105	ND[c]	70	ND	ND	ND	ND	730	1,858
Landscaping Refuse	Lab Stack	157	780	70	17	73	12	ND	ND	ND	505	1,614
Automobile Components	Lab Stack	13,000	34,300	6,570	1,180	8,900	1,000	1,090	1,420	9,690	24,400	101,550

[a] These ten POM compounds were specifically looked for during these tests. Conceivably others existed in the streams that were not identified. The POM compound abbreviations are keyed as follows: BaP - benzo(a)pyrene; P - pyrene; BeP - benzo(e)pyrene; Per - perylene; BghiP - benzo(g,h,i)perylene; Anth - anthanthrene; Cor - coronene; A - anthracene; Phen - phenanthrene; Fl - fluoranthene.

[b] Lab stack designates that POM measurements were made in a research laboratory designed to simulate open burning. Emissions from simulated open burning were collected by hooding and channeled through a stack for measurement. The sampling procedure in the lab stack tests was designed to collect both particulate and gaseous POM.

[c] ND designates that the compound was not detected.

TABLE 85. POM EMISSION FACTORS FOR THE OPEN BURNING OF MUNICIPAL REFUSE, AUTOMOBILES, AND LANDSCAPING REFUSE[82,169]

Type of Open Burning	Total POM and Benzo(a)pyrene Emission Factors: Total POM mg/kg of Waste Burned	Total POM and Benzo(a)pyrene Emission Factors: Benzo(a)pyrene mg/kg of Waste Burned
Municipal Refuse	0.5[a] - 4.7	0.088[a] - 0.340
Automobile Tires	240[a]	55[a]
Automobile Bodies	110[a]	14[a]
Automobile Components	190 - 260	20 - 29
Grass, Leaves, and Branches	2.5[a] - 9.2	0.30 - 0.35
Leaf Burning (red oak leaves)	11.2 - 78[b]	0.097 - 0.41[b,c]
Leaf Burning (sugar maple leaves)	12.0 - 18.7[b]	Not detected - 0.79[b,c]
Leaf Burning (sycamore leaves)	13.4 - 22.1[b]	0.27 - 0.54[b,c]
Leaf Burning (composite of red oak, sugar maple, and sycamore leaves)	10.2 - 21.8[b]	0.12 - 0.28[b,c]

[a] These emission factors were calculated from the smoke plume POM emission factors given in Table 83 (Reference 82) and the emission factors for total particulate matter emissions given in AP-42 for open burning. The AP-42 particulate emission factors used are as follows: municipal refuse - 8.0 kg/Mg; automobile components - 50 kg/Mg; landscaping refuse - 8.5 kg/Mg.

[b] Factors were developed by sampling at a leaf burning research facility using a glass fiber filter and a Tenax adsorber. Samples were analyzed by GC/MS. The POM compounds detected include anthracene/phenanthrene, methyl anthracenes, fluoranthene, pyrene, methyl pyrene/fluoranthene, benzo(c)-phenanthrene, chrysene/benz(a)anthracene, methyl chrysenes, benzo-fluoranthenes, benzo(a)pyrene/benzo(e)pyrene, perylene, methylcholanthrenes, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, dibenzo(c,g)carbazole, dibenzo(a,i and a,h)pyrenes, and coronene.

[c] Benzo(a)pyrene emission factors from these tests represent combined benzo(a)pyrene and benzo(e)pyrene emissions.

Although emission factors for POM from open burning of creosote railroad ties have not been quantified, this type of open burning has been shown to produce emissions containing several POM compounds.[171] The POM compounds that have been identified are listed below.[171]

- naphthalene
- acenaphthylene
- fluorene
- acenaphthene
- phenanthrene
- anthracene
- fluoranthene
- pyrene
- chrysene
- benz(a)anthracene
- benzo(b)fluoranthene
- benzo(k)fluoranthene
- benzo(a)pyrene
- dibenz(a,h)anthracene
- o-phenylenepyrene
- benzo(g,h,i)perylene

The predominant compounds measured were acenaphthene, acenaphthylene, benz(a)anthracene, benzo(a)pyrene, and dibenz(a,h)anthracene.

REFERENCES FOR SECTION 4

1. Shih, C., et al. POM Emissions from Stationary Conventional Combustion Processes, with Emphasis on Polychlorinated Compounds of Dibenzo-p-dioxin (PCDDs), Biphenyl (PCBs), and Dibenzofuran (DCDFs). CCEA Issue Paper presented under EPA Contract No. 68-02-3138. Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. January 1980.

2. Particulate Polycyclic Organic Matter. Committee on Biologic Effects of Atmospheric Pollutants, Division of Medical Sciences, National Research Council. National Academy of Sciences. Washington, D.C. 1972.

3. Polycyclic Aromatic Hydrocarbons: Evaluation of Sources and Effects. Committee on Pyrene and Selected Analogues, Board on Toxicology and Environmental Health Hazards, Commission on Life Sciences, National Research Council. National Academy Press, Washington, D.C. 1983.

4. Mead, R. C., G. W. Brooks, and B. K. Post. Summary of Trace Emissions from and Recommendations of Risk Assessment Methodologies for Coal and Oil Combustion Sources. Prepared under EPA Contract No. 68-02-3889, Work Assignment 41. Pollutant Assessment Branch, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. July 1986.

5. Hangebrauck, R. P., et al. Emissions of Polynuclear Hydrocarbons and Other Pollutants from Heat Generation and Incineration Processes. Journal of the Air Pollution Control Association. 14(7): 267-278. July 1964.

6. Kelly, M. E. Sources and Emissions of Polycyclic Organic Matter. EPA Report No. 450/5-83-010b. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1983. pp. 5-9 to 5-44.

7. Barrett, W. J., et al. Planning Studies for Measurement of Chemical Emissions in Stack Gases of Coal-fired Power Plants. EPRI Report No. EA-2892. Electric Power Research Institute, Palo Alto, California. 1983.

8. Griest, W. H. and M. R. Guerin. Identification and Quantification of Polynuclear Organic Matter (POM) on Particulates from a Coal-fired Power Plant. EPRI Report No. EA-1092. Electric Power Research Institute, Palo Alto, California. 1979.

9. Sonnichsen, T. W. Measurements of POM Emissions from Coal-fired Utility Boilers. EPRI Report No. CS-2885. Electric Power Research Institute, Palo Alto, California. 1983.

10. Haile, C. L., et al. Comprehensive Assessment of the Specific Compounds Present in Combustion Processes. EPA Report No. 560/5-83-006. Office of Pesticides and Toxic Substances, U. S. Environmental Protection Agency, Washington, D.C. 1983.

11. Shih, C. C. et al. Emissions Assessment of Conventional Stationary Combustion Systems, Volume III - External Combustion Sources for Electricity Generation. Prepared under EPA Contract No. 68-02-2197. Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1980.

12. Hangebrauck, R. P., et al. Sources of Polynuclear Hydrocarbons in the Atmosphere. Public Health Service Report No. AP-33. U. S. Department of Health, Education, and Welfare; Public Health Service. Cincinnati, Ohio. 1967. pp. 5-14.

13. Suprenant, N. F., et al. Emissions Assessment of Conventional Stationary Combustion Systems, Volume V - Industrial Combustion Sources. Prepared under EPA Contract No. 68-02-2197. Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1980.

14. McCurley, W. R., et al. Source Assessment: Dry Bottom Industrial Boilers Firing Pulverized Bituminous Coal. EPA Report No. 600/2-79-019e. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1979.

15. Burlingame, J. O., et al. Field Tests of Industrial Coal Stoker Fired Boilers for Inorganic Trace Element and Polynuclear Aromatic Hydrocarbon Emissions. EPA Report No. 600/7-81-167. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1981.

16. Suprenant, N. F., et al. Emission Assessment of Conventional Stationary Combustion Systems, Volume IV - Commercial/Industrial Combustion Sources. Prepared under EPA Contract No. 68-02-2197. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1980.

17. Giammar, R. D., et al. Emissions from Residential and Small Commercial Stoker Coal-fired Boilers Under Smokeless Operation. EPA Report No. 600/7-76-029. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1976.

18. DeAngelis, D. G. and R. B. Reznik. Source Assessment: Residential Combustion of Coal. EPA Report No. 600/2-79-019a. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. January 1979.

19. Sanborn, C. R., et al. Characterization of Emissions of PAHs from Residential Coal-fired Space Heaters. Paper presented at the 76th Annual Meeting of the Air Pollution Control Association, Atlanta, Georgia, June 19-24, 1983. Paper No. 83-54.4.

20. DeAngelis, R. and B. Piper. Particulate Emissions Characteristics of Oil-fired Utility Boilers - Phase II. KVB Report No. 1-21610-1107. KVB, Inc., Elmsford, New York. July 1981.

21. Zelenski, S. G., et al. Inventory of Organic Emissions from Fossil Fuel Combustion for Power Generation. EPRI Report No. EA-1394. Electric Power Research Institute, Palo Alto, California. April 1980.

22. Tennessee Valley Authority. Wood-fired Boiler Test Report - Down-Draft Boiler. TVA Report No. TVA/P&E/C&EM-85/13. Energy Use Test Facility, Chattanooga, Tennessee. October 1964.

23. Tennessee Valley Authority. Wood-fired Boiler Test Report - Stick Burner. TVA Report No. TVA/OP/ECR-84/4. Energy Use Test Facility, Chattanooga, Tennessee. August 1983.

24. Alsberg, T. and U. Stenberg. Capillary GC-MS Analysis of PAH Emissions from Combustion of Peat and Wood in a Hot Water Boiler. Chemosphere. 7: 487-496. 1979.

25. Wainwright, P. B., et al. A POM Emissions Study for Industrial Wood-fired Boilers. Division of Environmental Management, North Carolina Department of Natural Resources and Community Development, Raleigh, North Carolina. April 1982.

26. A Polycyclic Organic Materials Emissions Study for Industrial Wood-fired Boilers. NCASI Technical Bulletin No. 400. National Council of the Paper Industry for Air and Stream Improvement, New York, New York. May 1983.

27. Truesdale. R. S. Characterization of Emissions from a Fluidized-bed Wood Chip Home Heating Furnace. EPA Report No. 600/7-84-038. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. March 1984.

28. Peters, J. A. POM Emissions from Residential Woodburning: an Environmental Assessment. In: Proceedings of the 1981 International Conference on Residential Solid Fuels - Environmental Impacts and Solutions. Portland, Oregon. June 1-4, 1981. J. A. Cooper and D. Malek, eds. Oregon Graduate Center. Beaverton, Oregon. 1982.

29. DeAngelis, D. G., et al. Preliminary Characterization of Emissions from Wood-fired Residential Combustion Equipment. EPA Report No. 600/7-80-040. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. March 1980.

30. Hall, R. E. and D. G. DeAngelis. EPA's Research Program for Controlling Residential Wood Combustion Emissions. Journal of the Air Pollution Control Association. 30(8): 862-867. August 1980.

31. Hartman, M. W. and G. D. Rives. Literature Review and Survey of Emissions from Residential Wood Combustion and Their Impact. EPA Report No. 660/2-85-047. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. April 1985.

32. Peters, J. A., et al. An Environmental Assessment of POM Emissions from Residential Wood-fired Stoves and Fireplaces. In: Polynuclear Aromatic Hydrocarbons: Chemical Analysis and Biological Fate, Proceedings of the Fifth International Symposium on Polynuclear Aromatic Hydrocarbons, 1980, Columbus, Ohio. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. 1981.

33. Snowden, W. D., et al. Source Sampling Residential Fireplaces for Emission Factor Development. EPA Report No. 450/3-76-010. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. August 1975.

34. Lao, R. C., et al. Investigation of PAH and Polychlorinated Organic Pollutant Emissions from Wood Combustion Sources. In: Polynuclear Aromatic Hydrocarbons: Formation, Mechanism, and Measurement, Proceedings of the Seventh International Symposium on Polynuclear Aromatic Hydrocarbons, 1982, Columbus, Ohio. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. 1983.

35. Knight, C. V., et al. Polynuclear Aromatic Hydrocarbons and Associated Organic Emissions for Catalytic and Noncatalytic Wood Heaters. In: Polynuclear Aromatic Hydrocarbons: Formation, Mechanism, and Measurement, Proceedings of the Seventh International Symposium on Polynuclear Aromatic Hydrocarbons, 1982, Columbus, Ohio. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. 1983.

36. Tennessee Valley Authority. Residential Wood Heater Test Report - Phase I Testing. TVA Report No. TV/OP/ECR-83/4. Energy Use Test Facility, Chattanooga, Tennessee. November 1982.

37. Baladi, E. Stationary Source Testing of Bagasse-fired Boilers at the Hawaiian Commercial and Sugar Company, Puunene, Maui, Hawaii. MRI Report No. 3927-C(12). Midwest Research Institute, Kansas City, Missouri. February 1976.

38. Cooke, M., et al. Waste Oil Heaters: Organic, Inorganic, and Bioassay Analyses of Combustion Samples. EPA Report No. 600/D-84-130. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. May 1984.

39. Chansky, S., et al. Waste Automotive Lubricating Oil Reuse as a Fuel. EPA Report No. 600/5-74-032. U. S. Environmental Protection Agency, Washington, D.C. September 1974.

40. Energy Information Administration. State Energy Data Report, Consumption Estimates, 1960-1982. EIA Report No. DOE/EIA-0214(82). Energy Information Administration, Department of Energy, Washington, D.C. 1984.

41. Gibson, T. L., A. I. Ricci, and R. L. Williams. Measurement of Polynuclear Aromatic Hydrocarbons, Their Derivatives, and Their Reactivity in Diesel Automobile Exhaust. In: Polynuclear Aromatic Hydrocarbons: Chemical Analysis and Biological Fate, Proceedings of the Fifth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1980. M. Cooke and A. J. Dennis, eds. Battelle Press, Columbus, Ohio. 1981. pp. 707-717.

42. Reference 3, pp. 1-1 to 1-35.

43. Peake, E., and K. Parker. Polynuclear Aromatic Hydrocarbons and the Mutagenicity of Used Crankcase Oils. In: Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects. Proceedings of the Fourth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1979. A. Bjorseth and A. Dennis, eds. Battelle Press, Columbus, Ohio. 1980. pp. 1025-1039.

44. Handa, T., T. Yamamura, Y. Kato, S. Saito, and T. Ishii. Factor Analysis and Derivation of an Experimental Equation on Polynuclear Aromatic Hydrocarbon Emissions from Automobiles. Environmental Science and Technology. 13(9): 1077-1081. 1979.

45. Pederson, P. S., J. Ingwersen, T. Nielsen, and E. Larsen. Effects of Fuel, Lubricant, and Engine Operating Parameters on the Emission of Polycyclic Aromatic Hydrocarbons. Environmental Science and Technology. 14(1): 71-79. 1980.

46. U. S. Department of Transportation. Highway Statistics 1984. U. S. Government Printing Office, Washington, D.C. 1984.

47. Reference 2, pp. 15-21.

48. Reference 12, pp. 33-37.

49. Handa, T., T. Yamauchi, K. Sawai, T. Yamamura, Y. Koseki, and T. Ishii. In Situ Emission Levels of Carcinogenic and Mutagenic Compounds from Diesel and Gasoline Engine Vehicles on an Expressway. Environmental Science and Technology. 18(12): 895-902. 1984.

50. Hoffman, D., E. Theisz, and E. L. Wynder. Studies on the Carcinogenesis of Gasoline Exhaust. Journal of the Air Pollution Control Association. 15: 162-165. 1965.

51. Gross, G. P. Effects of PNA in Fuels. In: Third Annual Report on Gasoline Composition and Vehicle Exhaust Gas Polynuclear Aromatic Content. CRC-APRAC Project No. CAPE-6-68. Esso Research and Engineering Company, Linden, New Jersey. 1972. pp. 33-38.

52. Boubel, R. W., and L. A. Ripperton. Benzo(a)pyrene Production During Controlled Combustion. Journal of the Air Pollution Control Association. 13: 553-557. 1963.

53. Hoffman, D., and E. L. Wynder. Studies on Gasoline Engine Exhaust. Journal of the Air Pollution Control Association. 13: 322-327. 1963.

54. Begeman, C. R. Carcinogenic Aromatic Hydrocarbons in Automobile Effluents. In: Vehicle Emissions--Selected SAE Papers. Paper 440C presented January 1962 at the SAE Automotive Engineering Congress. Society of Automotive Engineers, New York. pp. 163-174. 1964.

55. Gross, G. P. First Annual Report on Gasoline Composition and Vehicle Exhaust Gas Polynuclear Aromatic Content. U. S. Department of Health, Education, and Welfare, Durham, North Carolina. 1970.

56. Hoffman, C. S., Jr., R. L. Willis, G. H. Patterson, and E. S. Jacobs. Polynuclear Aromatic Hydrocarbon Emission from Vehicles. Presented to the 160th National Meeting of the American Chemical Society, Los Angeles, California. 1971.

57. Begeman, C. R., and J. M. Colucci. Polynuclear Aromatic Hydrocarbon Emissions from Automotive Engines. SAE Paper 700469. Society of Automotive Engineers, Detroit, Michigan. 1970.

58. Spindt, R. S. Study of Polynuclear Aromatic Hydrocarbon Emissions from Heavy Duty Diesel Engines. Coordinating Research Council, Inc., New York, and U. S. Environmental Protection Agency, Office of Air and Waste Management, Ann Arbor, Michigan. 1974.

59. Levin, J., C. Nilsson, and A. Norstrom. Sampling and Analysis of Polycyclic Aromatic Hydrocarbons (PAH) From Two-Stroke Chain-Saw Engines. Chemosphere. 13(3): 427-435.

60. Robertson, D. J., R. H. Groth, and T. J. Blasko. Organic Content of Particulate Matter in Turbine Engine Exhaust. Journal of the Air Pollution Control Association. 30(3): 261-266. 1980.

61. Siebert, P. C., et al. Preliminary Assessment of the Sources, Control and Population Exposure to Airborne Polycyclic Organic Matter (POM) as Indicated by Benzo(a)pyrene (BaP). Prepared under EPA Contract No. 68-02-2836. Pollutant Strategies Branch, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. November 1978. pp. 20-117.

62. U. S. Environmental Protection Agency. Federal Register, 31(61) Part II, p. 5170 et seq., March 30, 1966.

63. Lang, J. M., L. Snow, R. Carlson, F. Black, R. Zweidinger, and S. Tejada. Characterization of Particulate Emissions from In-Use Gasoline-Fueled Motor Vehicles. SAE Paper 811186. Society of Automotive Engineers, Warrendale, Pennsylvania. 1981.

64. Handa, T., Y. Kato, T. Yamamura, T. Ishii, and J. Matsushita. In-Situ Emission Levels of Polynuclear Aromatic Hydrocarbons from Gasoline and Diesel Engine Vehicles on an Expressway. Journal of Environmental Science and Health. A15(6): 573-599. 1980.

65. Lee, F., and D. Schuetzle. Sampling, Extraction, and Analysis of PAH from Internal Combustion Engines. In: Handbook of Polycyclic Hydrocarbons, A. Bjorseth, ed. Marcel Dekker Publishing Company. 1981.

66. Grimmer, G. Analysis of Automobile Exhaust Condensates. In: Air Pollution and Cancer in Man. IARC Scientific Publication No. 16. International Agency for Research on Cancer, Lyon, France. U. Mohr et al., eds. pp. 24-39. 1977.

67. Grimmer, G., H. Boehnke, and A. Glaser. In: Polycyclic Aromatic Hydrocarbons in Automobile Exhaust Gas - An Inventory. Investigation on the Carcinogenic Burden by Air Pollution in Man. Zentralbl. Bakteriol., Parasitenk., Infektionskr. Hyg., Abt. I: Orig., Reihe B 164: 218-234. 1977.

68. Kraft, J., and K. H. Lies. Polycyclic Aromatic Hydrocarbons in the Exhaust of Gasoline and Diesel Vehicles. SAE Paper 810082. Society of Automotive Engineers, Warrendale, Pennsylvania. 1981.

69. Tejada, S. Particulate NO_2-Pyrene Emissions from a 1980 Oldsmobile and 1980 VW Diesel, FTP and HWFET Cycles. Unpublished data. Cited in Reference 63. 1981.

70. Dietzmann, H. E., M. A. Parness, and R. L. Bradow. Emissions from Gasoline and Diesel Delivery Trucks by Chassis Transient Cycle. Presented at the Energy-Sources Technology Conference and Exhibition, January 18-22, Houston, Texas. 1981.

71. U. S. Environmental Protection Agency. Federal Register 45(14), p. 4161 et seq., January 21, 1980.

72. Williams, R. L., and S. J. Swarin. Benzo(a)pyrene Emissions from Gasoline and Diesel Automobiles. SAE Paper Presented at the Congress and Exposition. Cobo Hall, Detroit, Michigan, February 26 - March 2, 1979.

73. Gibson, T. L. Preliminary Communication: Nitro Derivatives of Polynuclear Aromatic Hydrocarbons in Airborne and Source Particulate Matter. Atmospheric Environment. 16(8): 2037-2040. 1982.

74. Choudhury, D. R., and B. Bush. Polynuclear Aromatic Hydrocarbons in Diesel Emission Particulates. In: Health Effects of Diesel Engine Emissions: Proceedings of an International Symposium - Vol. I. December 3-5, 1979. W. E. Pepelko et al., eds. U. S. Environmental Protection Agency, Cincinnati, Ohio.

75. Bricklemyer, B. A., and R. S. Spindt. Measurement of Polynuclear Aromatic Hydrocarbons in Diesel Exhaust Gases. SAE Technical Paper Presented at the Congress and Exposition. Cobo Hall, Detroit, Michigan, February 27 - March 3, 1978.

76. Lee, F., T. J. Prater, and F. Ferris. PAH Emissions from a Stratified-Charge Vehicle With and Without Oxidation Catalyst: Sampling and Analysis Evaluation. In: Polynuclear Aromatic Hydrocarbons, Proceedings of the Third International Symposium on Chemistry and Biology - Carcinogenesis and Mutagenesis. P. W. Jones and P. Leber, eds. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan. 1979. pp. 83-110.

77. Du, C. J., D. B. Kittelson, and R. B. Zweidinger. Measurements of Polycyclic Aromatic Compounds in the Cylinder of an Operating Diesel Engine. Prepared for U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1985.

78. Robertson, D. J., R. H. Groth, and T. J. Blasko. Organic Content of Particulate Matter in Turbine Engine Exhaust. Journal of the Air Pollution Control Association. 30(3): 261-266. 1980.

79. Reference 6, pp. 5-75 to 5-82.

80. Municipal Waste Combustion Study Data Gathering Phase. Radian Corporation. Prepared under EPA Contract No. 68-02-3818, Work Assignment 31. Pollutant Assessment Branch, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. July 1986.

81. Background Information Document for Cadmium Emission Sources. Radian Corporation. Prepared under EPA Contract No. 68-02-3818, Work Assignment 23. Pollutant Assessment Branch, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. May 1985. pp. 106-145.

82. Reference 12, pp. 14-18.

83. Haile, C. L., et al. Pilot Study of Information of Specific Compounds from Combustion Sources. EPA Report No. 560/5-83-004. Office of Toxic Substances, U. S. Environmental Protection Agency, Washington, D.C. June 1983.

84. Huynh, C. K., et al. In-stack Dilution Technique for the Sampling of Polycyclic Organic Compounds, Application to Effluents of a Domestic Waste Incineration Plant. Atmospheric Environment. 18(2): 255-259. 1984.

85. Eklund, G. and B. Stromberg. Detection of Polychlorinated Polynuclear Aromatics in Flue Gases from Coal Combustion and Refuse Incinerators. Chemosphere. 12(4): 657-660. 1983.

86. Clayton, P. The Incineration of Municipal Refuse. Warren Spring Laboratory, Stevenage, England. 1984.

87. Haile, C. L., et al. Assessment of Emissions of Specific Compounds from a Resource Recovery Municipal Refuse Incinerator. EPA Report No. 560/5-84-002. Office of Toxic Substances, U. S. Environmental Protection Agency, Washington, D.C. June 1984.

88. Reference 1, pp. 17-21.

89. U. S. Environmental Protection Agency. Second Review of Standards of Performance for Sewage Sludge Incinerators. Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. March 1984.

90. Bridle, T. R. Assessment of Organic Emissions from the Hamilton Sewage Sludge Incinerator. Environment Canada, Burlington, Ontario, Canada. 1982.

91. Lao, R. C., et al. Analysis of PAH and Organic Compounds in Environmental Samples. In: Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods, and Metabolism, Proceedings of the Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1983. M. Cooke and A. J. Dennis, eds. Battelle Press, Columbus, Ohio. 1985.

92. U. S. Environmental Protection Agency. Seminar Publication: Municipal Wastewater Sludge Combustion Technology. EPA Report No. 625/4-85-015. U. S. Environmental Protection Agency, Cincinnati, Ohio. September 1985.

93. Letter and attachments from Knight, L., Eastern Research Group to Dykes, R. M., Radian Corporation. April 16, 1986. List of water treatment plants with sewage sludge incinerators.

94. Reference 81, pp. 71-83.

95. Radian Corporation. Assessment of Atmospheric Emissions from Petroleum Refining. EPA Report No. 600/2-80-075E. Industrial Environment Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. July 1980. pp. 192-203.

96. Reference 2, pp. 26-27.

97. Reference 12, pp. 18-25.

98. Cantrell, A. Annual Refining Survey. Oil and Gas Journal. 83(11): 122-137. March 24, 1986.

99. Reference 6, pp. 5-58 to 5-62.

100. GCA Corporation. Survey of Cadmium Emission Sources. EPA Report No. 450/3-81-013. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. September 1981.

101. U. S. Environmental Protection Agency. An Investigation of the Best Systems of Emission Reduction for Sinter Plants in the Iron and Steel Industry. Preliminary Report. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. May 1977.

102. Reference 61, pp. 78-79.

103. U. S. Environmental Protection Agency. A Review of Standards of Performance for New Stationary Sources - Ferroalloy Production Facilities. EPA Report No. 450/3-80-041. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. December 1980.

104. U. S. Environmental Protection Agency. Background Information for Standards of Performance: Electric Submerged Arc Furnaces for Production of Ferroalloys, Volume I: Proposed Standards. EPA Report No. 450/2-74-018a. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1974.

105. U. S. Environmental Protection Agency. Locating and Estimating Air Emissions from Sources of Chromium. EPA Report No. 450/4-84-007g. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. July 1984.

106. Brown, R. E. Ferroalloys. In: 1984 Bureau of Mines Minerals Yearbook. Bureau of Mines, U. S. Department of Interior. U. S. Government Printing Office, Washington, D.C. 1985.

107. U. S. Environmental Protection Agency. Electric Arc Furnaces in Ferrous Foundries - Background Information for Proposed Standards. EPA Report No. 3-80-020a. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. May 1980.

108. Verma, D. K., et al. Polycyclic Aromatic Hydrocarbons in Ontario Foundry Environments. Annals of Occupational Hygiene. 25(1): 17-25. 1982.

109. Schimberg, R. W. Polycyclic Aromatic Hydrocarbons in Foundries. Journal of Toxicology and Environment Health. 6(5-6): 1187-1194. September/November 1980.

110. Quilliam, M. A., et al. Identification of Polycyclic Aromatic Compounds in Mutagenic Emissions from Steel Casting. Biomedical Mass Spectrometry. 12(4): 143-150. 1985.

111. McCalla, D. R., et al. Formation of Bacterial Mutagens from Various Mould Binder Systems Used in Steel Foundries. In: Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods, and Metabolism, Proceedings of the Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1983. M. Cooke and A. J. Dennis, eds. Battelle Press, Columbus, Ohio. 1985. pp. 871-884.

112. U. S. Environmental Protection Agency. Coke Oven Emissions from Wet-Coal Charged By-product Coke Oven Batteries - Background Information for Proposed Standards. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. August 1985.

113. Van Osdell, D. W., et al. Environmental Assessment of Coke By-product Recovery Plants. EPA Report No. 600/2-79-016. Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. January 1979.

114. Reference 6, pp. 5-46 to 5-56.

115. Barrett, R. E., et al. Effectiveness of a Wet Electrostatic Precipitator for Controlling POM Emissions from Coke Oven Door Leakage. Paper presented at the 71st Annual Meeting of the Air Pollution Control Association, Houston, Texas, June 25-30, 1978. Paper No. 78-9.3.

116. Reference 3, pp. 2-23 to 2-26.

117. U. S. Environmental Protection Agency. Carcinogen Assessment of Coke Oven Emissions. EPA Report No. 600/6-82-003F. Office of Health and Environmental Assessment, U. S. Environmental Protection Agency, Washington, D.C. February 1984. pp. 6-11.

118. Reference 61, pp. 64-71

119. Eisenhut, W., et al. Determination of PAH Pollution at Coke Works. In Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry, Proceedings of the Sixth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1981. M. Cooke, A. J. Dennis, and G. L. Fisher, eds. Battelle Press, Columbus, Ohio. 1982. pp. 255-261.

120. Lao, R. C., et al. Computerized Gas Chromatographic-Mass Spectrometric Analysis of Polycyclic Aromatic Hydrocarbons in Environmental Samples. Journal of Chromatography. 112: 681-700. 1975.

121. U. S. Environmental Protection Agency. Asphalt Roofing Manufacturing Industry - Background Information for Proposed Standards. EPA Report No. 450/3-80-021a. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. June 1980.

122. Reference 6, pp. 5-62 to 5-72.

123. Gerstle, R. W. Atmospheric Emissions from Asphalt Roofing Processes. EPA Report No. 650/2-74-101. Control Systems Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1974.

124. Reference 61, pp. 72-78.

125. Reference 12, pp. 25-26.

126. Letter from the Asphalt Roofing Manufacturers Association to Cruse, P., Radian Corporation. June 11, 1986. List of asphalt roofing manufacturing plants.

127. U. S. Environmental Protection Agency. Second Review of New Source Performance Standards for Asphalt Concrete Plants. EPA Report No. 450/3-85-024. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1985.

128. Reference 6, pp. 5-63 to 5-68.

129. Khan, Z. S., et al. Polycyclic Organic Material Emissions from Asphalt Hot Mix Plants. Paper presented at the 70th Annual Meeting of the Air Pollution Control Association, Toronto, Ontario, Canada. June 20-24, 1977. Paper No. 77-16.4.

130. Reference 12, pp. 27-28.

131. Reference 61, pp. 72-76.

132. Fuchs, M. R., et al. Emission Test Report: T. J. Campbell Asphalt Concrete Plant, Oklahoma City, Oklahoma. EPA/EMB Report No. 83-ASP-4. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. May 1984.

133. Serth, R. W. and T. W. Hughes. Polycyclic Organic Matter (POM) and Trace Element Contents of Carbon Black Vent Gas. Environmental Science and Technology 14(3): 298-301. March 1980.

134. Serth, R. W. and T. W. Hughes. Source Assessment: Carbon Black Manufacture. EPA Report No. 600/2-77-107k. Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1977.

135. Reference 6, pp. 5-85 to 5-88.

136. Reference 61, pp. 80-82.

137. Miller, S. E. and R. E. Barrett. Sampling and Analysis of Source Emission Samples from a Carbon Black Plant. EPA/EMB Report No. 75-CBK-2. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. May 1975.

138. 1985 SRI Directory of Chemical Producers - United States of America. SRI International, Menlo Park, California. 1985. p. 477.

139. Reference 3, p. 2-35.

140. Bennett, R. L., et al. Measurement of Polynuclear Aromatic Hydrocarbons and Other Hazardous Organic Compounds in Stack Gases. In: Polynuclear Aromatic Hydrocarbons: Chemistry and Biology - Carcinogenesis and Mutagenesis, Proceedings of the Third International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1978. P. W. Jones and P. Leber, eds. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan. 1979.

141. Rives, G. D. and A. J. Miles. Control of Arsenic Emissions from the Secondary Lead Smelting Industry - Technical Document. Prepared under EPA Contract No. 68-02-3816. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. May 1985.

142. U. S. Environmental Protection Agency. Primary Aluminum Draft Guidelines for Control of Fluoride Emissions from Existing Primary Aluminum Plants. EPA Report No. 450/2-78-049a. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. February 1979.

143. Reference 61, pp. 82-85.

144. Wallingford, K. M. and S. S. Que Hee. Occupational Exposure to Benzo(e)pyrene. In: Polynuclear Aromatic Hydrocarbons: Mechanisms Methods, and Metabolism, Proceedings of the Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1983. M. Cooke and A. J. Dennis, eds. Battelle Press, Columbus, Ohio. 1985.

145. Alfheim, I. and Wikstrom, L. Air Pollution from Aluminum Smelting Plants 1. The Emission of Polycyclic Aromatic Hydrocarbons and of Mutagens from an Aluminum Smelting Plant Using the Soderberg Process. Toxicological and Environmental Chemistry 8(1): 55-72. 1984.

146. Reference 138, p. 412.

147. Reference 6, pp. 5-89 to 5-93.

148. Moscowitz, C. W. Source Assessment: Charcoal Manufacturing - State-of-the-Art. EPA Report No. 600/2-78-004z. Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. December 1978.

149. U. S. Department of Agriculture. The Biologic and Economic Assessment of Pentachlorophenol, Inorganic Arsenicals, and Creosote - Volume I: Wood Preservatives. USDA Technical Bulletin No. 1658-1. U. S. Department of Agriculture, Washington, D.C. November 1980.

150. Andersson, K., et al. Sampling and Analysis of Particulate and Gaseous Polycyclic Aromatic Hydrocarbons from Coal Tar Sources in the Working Environment. Chemosphere. 12(2): 197-207. 1983.

151. Micklewright, J. T. Wood Preservation Statistics, 1983 and 1984. International Statistics Council. Published by the American Wood Preservers Institute, McLean, Virginia. 1985.

152. Olsen, K. B., et al. Analysis and Collection of PAHs in the Flue Gas of Energy Conversion Facilities. In: Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods, and Metabolism, Proceedings of the Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1983. M. Cooke and A. J. Dennis, eds. Battelle Press, Columbus, Ohio. 1985.

153. Natusch, D. F. Formation and Transformation of Particulate Polycyclic Organic Matter Emitted from Coal Fired Power Plants and Oil Shale Retorting. DOE Report No. DE84-012747, DOE/EV/04960-TI. U. S. Department of Energy, Washington, D.C. April 1984.

154. Taylor, R. B. Oil Shale Commercialization: The Risks and the Potential. Chemical Engineering. 88(18): 63-71. September 7, 1981.

155. Bates, E. R. and T. L. Thoem, eds. Environmental Perspective on the Emerging Oil Shale Industry. EPA Report No. 600/2-8-205a. Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1980.

156. Telephone conversation between Ramsey, M. R., U. S. Department of Energy and Brooks, G. W., Radian Corporation. January 13, 1986. Existence of commercial oil shale retorting operations in the United States.

157. Eldridge, J. E., et al. PAH Emissions from Paving Asphalt in Laboratory Simulation. In: Polynuclear Aromatic Hydrocarbons: Formation, Metabolism, and Measurement, Proceedings of the Seventh International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1982. M. Cooke and A. J. Dennis, eds. Battelle Press, Columbus, Ohio. 1983. pp. 471-482.

158. Malaiyandi, M., et al. Measurement of Potentially Hazardous Polynuclear Aromatic Hydrocarbons from Occupational Exposure During Roofing and Paving Operations. In: Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry, Proceedings of the Sixth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1981. M. Cooke, A. J. Dennis, and G. L. Fisher, eds. Battelle Press, Columbus, Ohio. 1982. pp. 471-489.

159. Reed, L. D. and Liss, G. M. PAH Exposures Among Pitch and Asphalt Roofing Workers. In: Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods, and Metabolism, Proceedings of the Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1983. M. Cooke and A. J. Dennis, eds. Battelle Press, Columbus, Ohio. 1985. pp. 1089-1095.

160. Gorman, R. and G. M. Liss. Occupational Exposure to Pitch in a Non-heated Process - Photoxicity and Pre-malignant Warts. In: Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods, and Metabolism, Proceedings of the Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1983. M. Cooke and A. J. Dennis, eds. Battelle Press, Columbus, Ohio. 1985. pp. 497-508.

161. Chalekode, P. K. and T. R. Blackwood. Source Assessment: Coal Refuse Piles, Abandoned Mines, and Outcrops - State of the Art. EPA Report No. 600/2-78-004v. Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio. July 1978.

162. Reference 6, pp. 5-3 to 5-9.

163. Chi, C. T., et al. Source Assessment: Prescribed Burning, State of the Art. EPA Report No. 600/2-79-019h. Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. November 1979.

164. Reference 61, pp. 99-102.

165. McMahon, C. K. and S. N. Tsoukalas. Polynuclear Aromatic Hydrocarbons in Forest Fire Smoke. In: Polynuclear Aromatic Hydrocarbons: Analysis, Chemistry, and Biology, Proceedings of the Second International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1977. P. W. Jones and R. I. Freudenthal, eds. Raven Press, New York. 1978. pp. 61-73.

166. Telephone conversation between Cruse, P. A., Radian Corporation and Eubanks, R., U. S. Forest Service. June 11, 1986. Listing of prescribed burning acreage by Forest Service region for the United States.

167. Information submitted to Cruse, P. A., Radian Corporation by Hansen, K., U. S. Forest Service. June 23, 1986. Forest Service reports on wildfire statistics for 1978 to 1983.

168. Chi, C. T. and D. L. Zanders. Source Assessment: Agricultural Open Burning, State of the Art. EPA Report No. 600/2-77-107a. Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. July 1977.

169. Reference 61, pp. 92-97.

170. Reference 6, pp. 5-93 to 5-95.

171. Becker, D., et al. Open Burning of Creosote Treated Rail Ties: A Case Study in Health Risk Assessment. Paper presented at the 77th Annual Meeting of the Air Pollution Control Association, San Francisco, California, June 24-29, 1984. Paper No. 84-102.6.

172. Municipal Waste Combustion Study. Emission Data Base for Municipal Waste Combustors. EPA/530-SW-87-021b. U. S. Environmental Protection Agency. Washington, D.C. June 1987.

SECTION 5

SOURCE TEST PROCEDURES

Several sampling and analysis techniques have been employed for the quantification of POM. The selection of sampling and analytical techniques is driven by the nature of the emissions source, the quantity of POM present, and the specific POM compounds of interest. With the exception of real time techniques, quantification of POM involves three steps: (1) sample collection, (2) sample recovery and preparation, and (3) quantitative analysis. This section briefly describes general methodologies associated with each of these steps that have been published in the literature. No attempt has been made to produce an exhaustive listing or a detailed description of the many methodologies that have been used. The purpose of this section is to present basic sampling and analysis principles and examples of how these principles have been applied to various emission sources. The presentation of these published methods in this report does not constitute endorsement or recommendation or signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency.

SAMPLE COLLECTION METHODS

The major objective of POM measurement is the quantitative capture and recovery of both particle-bound and vapor phase constituents, while simultaneously preserving the integrity of the sample. A second important factor in sample collection is the ability to capture sufficient quantities to allow subsequent chemical analysis. Although collection methods take different forms, most are similar in principle, utilizing both filtration and adsorption collection techniques. This section presents an overview of some of the more prevalent POM sample collection methods as applied to (1) stationary sources, (2) mobile sources, and (3) fugitive sources and/or ambient air.

Stationary Sources--

Collection of POM material from stationary sources is generally achieved by using a sampling system that captures both particulate and condensables.[1-4] The most prevalent method is the Modified Method 5 Sampling Train (MM5) which is equipped with a sorbent resin for collection of condensables. Another method, the Source Assessment Sampling System (SASS), a high volume variation of MM5, has found application when large sample sizes are required. Methods which are not specifically designed to optimize collection of condensables have also been used and are reported in the literature.[4,5] A brief description of the MM5 and the SASS trains is provided. General characteristics of each method are compared in Table 86.[6] A detailed procedures manual describing each of these methods is available in a separate report.[6]

Modified Method 5 (MM5)--The MM5 sampling train (shown in Figure 40) is an adaptation of the EPA Method 5 train commonly used in measuring particulate emissions.[7] The modifications are the addition of a condensor and a sorbent module between the filter and the impingers. The condensor cools the gas stream leaving the filter and conditions the streams prior to entering the sorbent module. The sorbent module contains a polymer resin designed to adsorb a broad range of volatile organic species. A variety of resins have been used including Tenax, Chromsorb 102, and XAD-2, with XAD-2 being the most widely recommended for vapor phase organic compounds including POM.[8] After the sorbent trap, the sample gas is routed through impingers, a pump, and a dry gas meter. The MM5 train is designed to operate at flow rates of approximately 0.015 dscmm (0.5 dscfm) over a 4 hour sampling period. Sample volumes of 3 dscm (100 dscf) are typical.

A major advantage of the MM5 train is that the method provides both a quantitative sample for POM analysis and a determination of particulate loading (front half filterable particulates) comparable to EPA Method 5. A disadvantage is that large sampling periods are required to collect enough sample to support chemical analysis.

TABLE 86. COMPARISON OF MODIFIED METHOD 5 TRAIN/SASS CHARACTERISTICS[6]

Characteristic	MM5 Train	SASS
Inert materials of construction	Yes	No
Percent isokinecity achievable	90 - 110	70 - 150[a]
Typically used to traverse	Yes	No
Particle-sizing of sample	No	Yes
Sample size over a 4-6 hour period (dscm)	3	30
Sampling flowrate (dscmm)	0.02 - 0.03	0.09 - 0.14

[a] Assuming reasonably uniform, non-stratified flow.

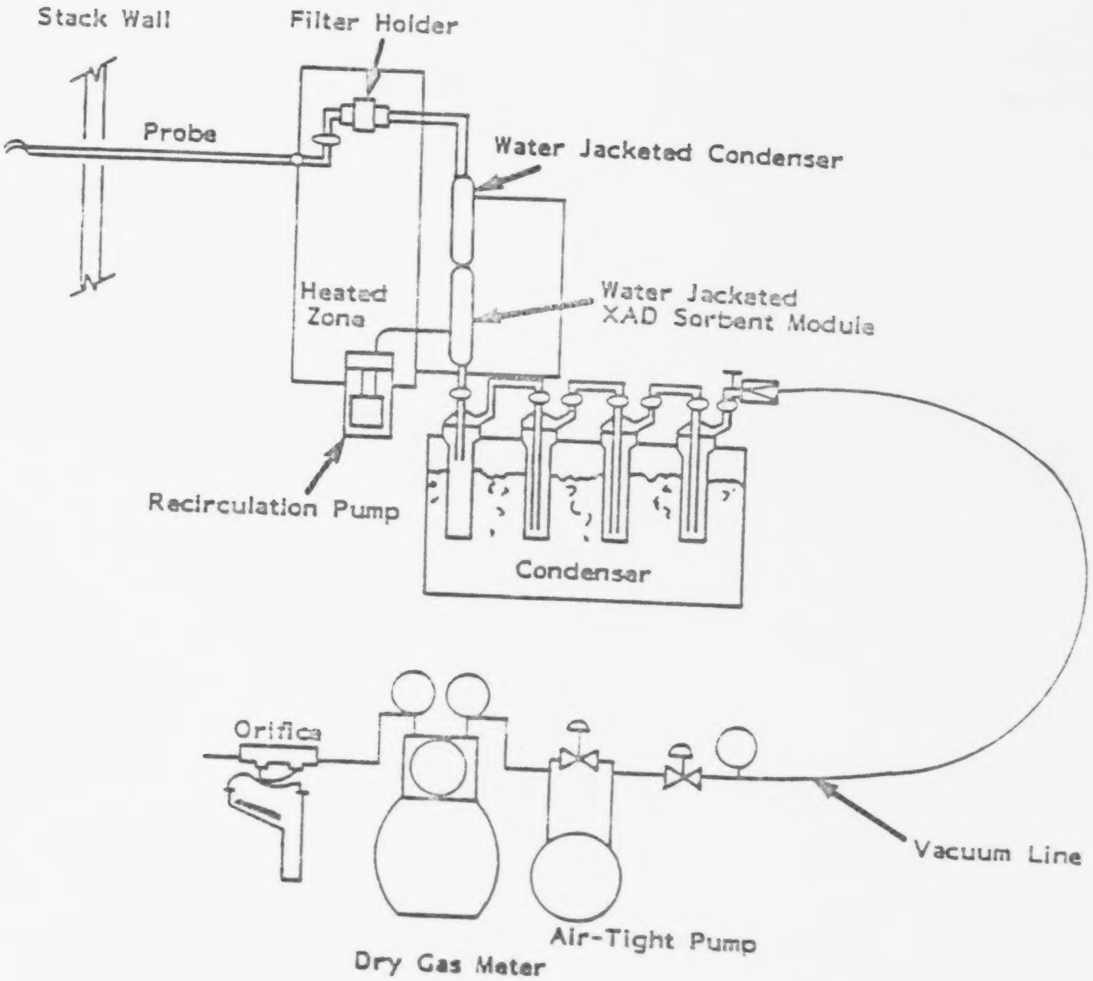

Stack Wall
Filter Holder
Probe
Water Jacketed Condenser
Heated Zone
Water Jacketed XAD Sorbent Module
Recirculation Pump
Condenser
Orifice
Vacuum Line
Air-Tight Pump
Dry Gas Meter

Figure 40. Schematic of a Modified Method 5 sampling train.

Source Assessment Sampling System (SASS)--The SASS train (shown in Figure 41)[9] is a multi-component sampling system designed for the collection of particulate, volatile organics and trace metals. Three heated cyclones and a heated filter allow size fractionation of the particulate sample. Volatile organic material is collected in a sorbent trap containing XAD-2 resin. Volatile inorganic species are collected in a series of impingers before the sample gas exits the system through a pump and a dry gas meter. Large sample volumes are required to ensure adequate recovery of sample fractions. The system is designed to operate at a flow rate of 0.113 scmm (4.0 scfm). Sample volumes of 30 dscm (1000 dscf) are typical.

An advantage of the SASS train is that the sample is collected in a manner that allows a determination of the amount of POM associated with each of the particle size fractions. Another advantage is the large quantity of sample collected, which makes SASS the sampler of choice when a large variety of chemical and bioassay analyses are desired. A disadvantage to using the SASS train is that the system is not designed to have the ability to traverse the stack. Also, the need for constant flow to assure proper size fractionation renders the SASS train less amenable for compliance determinations since isokinetic conditions are not achieved. Isokinetic conditions can be maintained at the sacrifice of particle sizing capability. Another drawback includes potential corrosion of the stainless steel components of the SASS train by acidic stack gases.

Mobile Sources--

Two general approaches have been used for sampling vehicle exhaust POM. The first and most widely used is a dilution tube sampling arrangement identical to the system used for measuring criteria pollutants from mobile sources.[10-12] The second approach involves direct sampling of raw exhaust gases using condensation techniques.[12,13] The following subsections provide an overview of each of these approaches.

Dilution Techniques--Dilution techniques have been widely used for sampling auto exhaust since in theory, dilution helps simulate the conditions under which exhaust gases condense and react in the atmosphere.

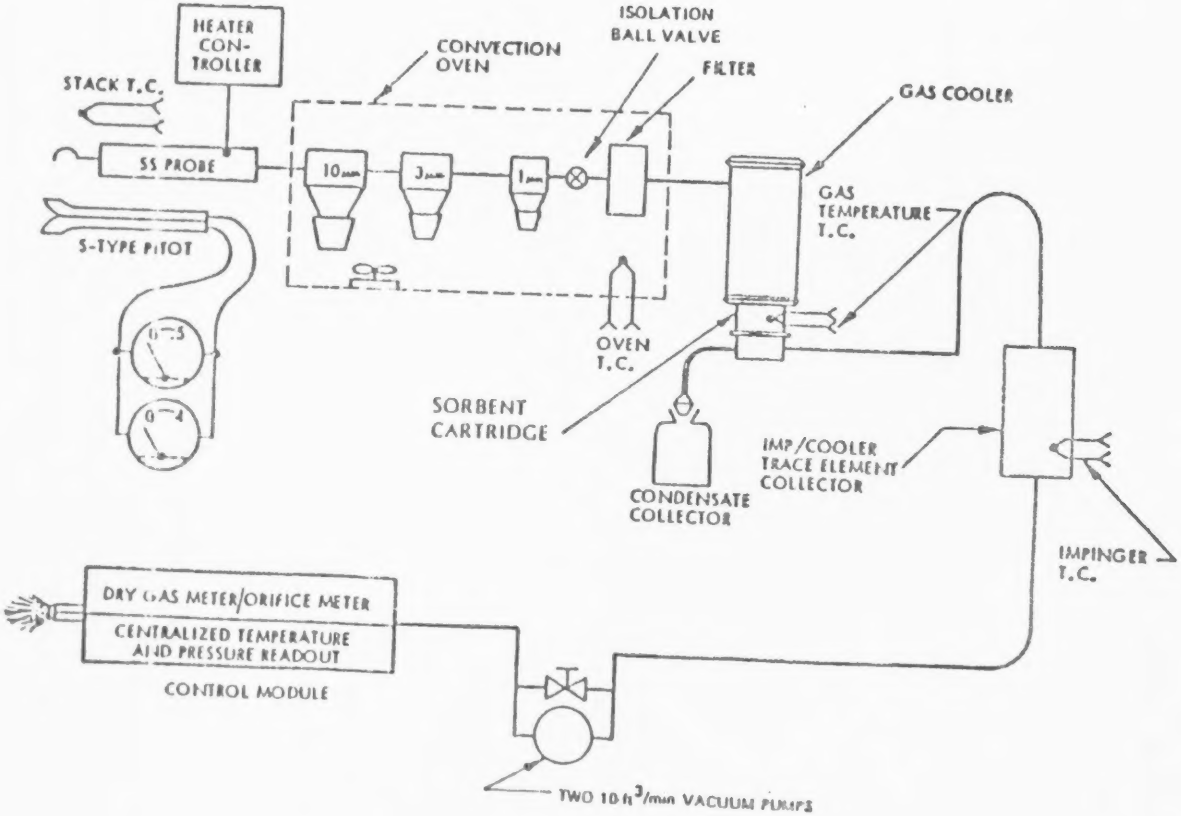

HEATER CON- TROLLER
STACK T.C.
SS PROBE
S-TYPE PITOT
CONVECTION OVEN
10µm
3µm
1µm
ISOLATION BALL VALVE
FILTER
OVEN T.C.
GAS COOLER
GAS TEMPERATURE T.C.
SORBENT CARTRIDGE
CONDENSATE COLLECTOR
IMP/COOLER TRACE ELEMENT COLLECTOR
IMPINGER T.C.
DRY GAS METER/ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
TWO 10 ft³/min VACUUM PUMPS

Figure 41. Schematic of a SASS sampling train.[9]

Both regulated and nonregulated emissions from mobile sources are sampled using dilution techniques.[10,11,14] Figure 42 shows a diagram of a vehicle exhaust dilution tube and sampling arrangement.[12] Vehicle exhausts are introduced at an orifice where the gases are cooled and mixed with a supply of filtered dilution air. The diluted exhaust stream flows at a measured velocity through the dilution tube and is sampled isokinetically. Many investigators have reported particulate-bound POM concentrations based on filter samples collected from the diluted exhaust stream.[15-18] Other investigators have coupled filtration and adsorption techniques for the purpose of capturing both gas phase and particulate bound POM.[19-21] Table 87 shows a distribution of particulate bound and gas phase POM collected from vehicle exhaust.[22] As seen in the table, and confirmed by other investigators, substantial amounts of light three and four ring POMs (as polycyclic aromatic hydrocarbons) exist in the gas phase.[22,23] An example of a filtration/adsorption sampling arrangement is shown in Figure 43.[24] Particle-bound POM is captured by filtration, while a polymeric adsorbent trap located downstream of the filter collects gas phase constituents. Commonly used adsorbent resins include XAD-2, Chromsorb 102, and Tenax.[19]

The major advantage in using a dilution tube approach is that exhaust gases are allowed to react and condense onto particle surfaces prior to sample collection, providing a truer composition of exhaust emissions as they occur in the atmosphere. Other advantages are that the dilution tube sampling arrangement is the reference method for sampling regulated pollutants from vehicle exhaust, and the dilution tube configuration allows simultaneous monitoring of hydrocarbons, carbon monoxide, carbon dioxide, and nitrogen oxides. Polycyclic organic matter sampling devices used in conjunction with dilution tube arrangements may consist only of filters for collection of particle bound POM (compounds with five or more rings are expected to be associated with particulate), or filtration/adsorption techniques may be used for the collection of both particulate and gas phase POM. Back-up adsorption techniques are generally recommended for complete capture of POM because even particle bound POM will readily volatilize from a filter and pass through in the sample air stream.

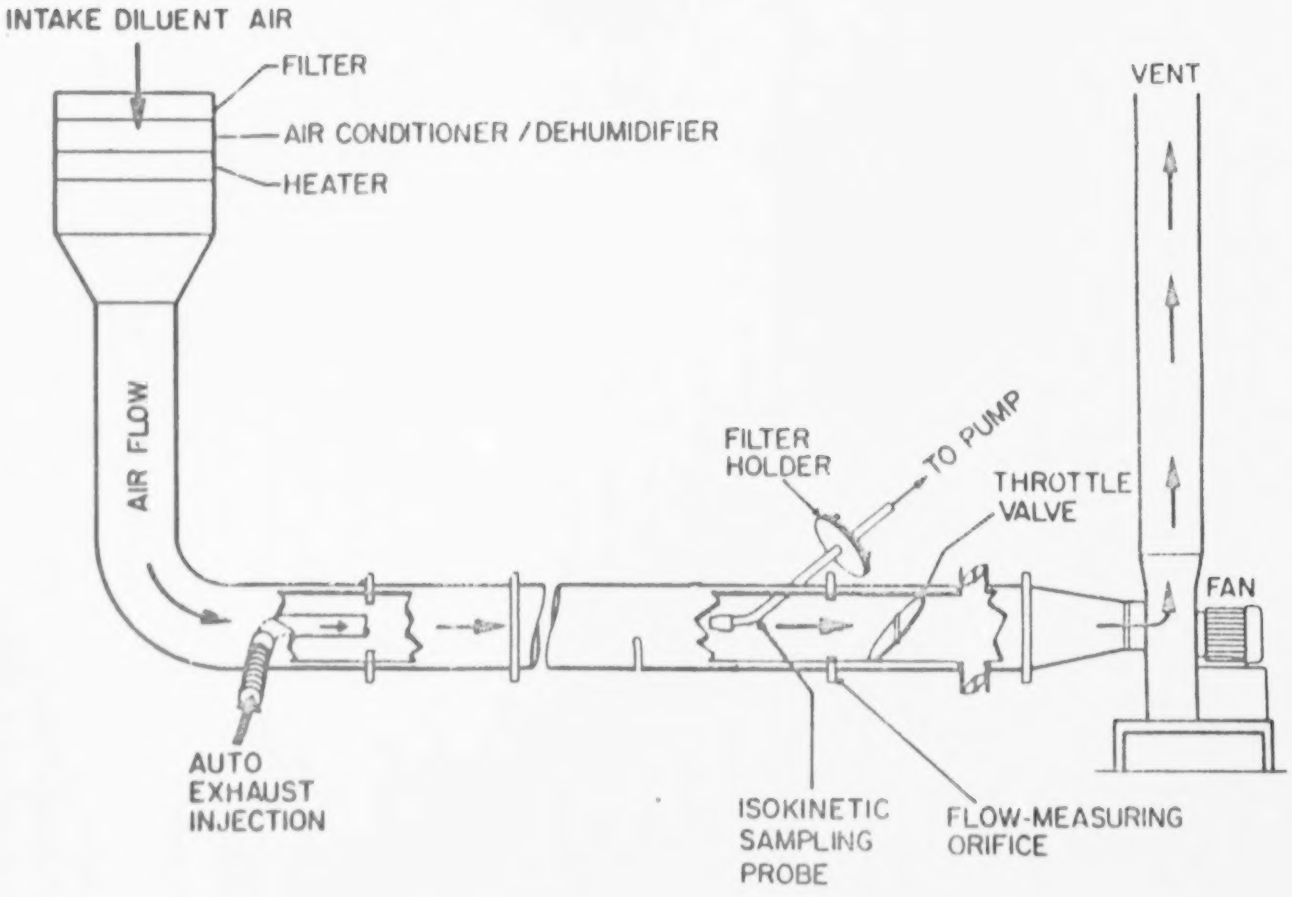

INTAKE DILUENT AIR
FILTER
AIR CONDITIONER / DEHUMIDIFIER
HEATER
AIR FLOW
AUTO EXHAUST INJECTION
FILTER HOLDER
TO PUMP
THROTTLE VALVE
VENT
FAN
ISOKINETIC SAMPLING PROBE
FLOW-MEASURING ORIFICE

Figure 42. Diagram of a vehicle exhaust dilution sampling arrangement.

TABLE 87. DISTRIBUTION OF POM IN THE PARTICULATE AND GAS PHASE FROM VEHICLE EXHAUST.[22]

POM	Micrograms/Sample	
	Filter	XAD Trap
Phenanthrene	40	16
Anthracene	8	30
Fluoranthene	34	30
Pyrene	36	40
Chrysene + benz(a)anthracene	70	50
Benzo(e)pyrene	28	0.1
Benzo(a)pyrene	9	0.1
Benzo(g,h,i)perylene	31	0.2
Picene + dibenzoanthracenes	9	0.2
Anthanthrenes	13	0.2
Dibenzopyrene	3	0.2
Coronene	4	0.2

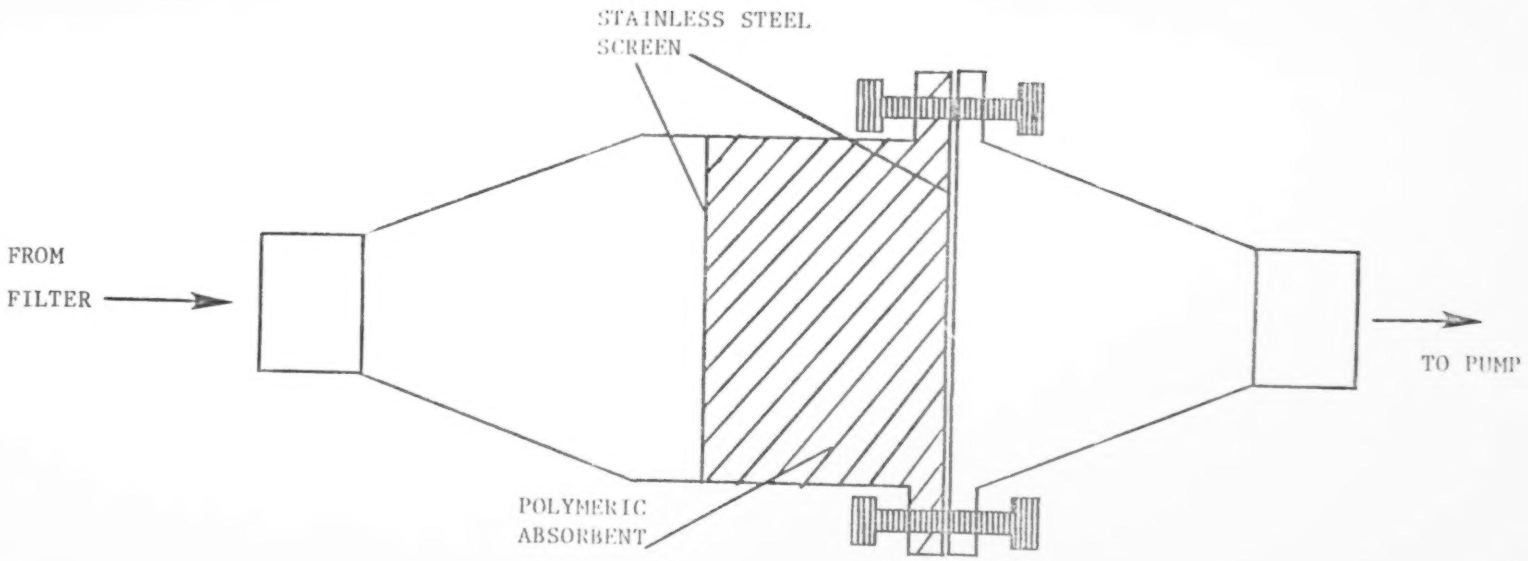

STAINLESS STEEL
SCREEN
FROM
FILTER
TO PUMP
POLYMERIC
ABSORBENT

Figure 43. Adsorbent trap for the collection of gas-phase POM from vehicle exhaust.

Condensation Techniques--Polycyclic organic matter emissions from vehicle exhausts have also been collected using cryogenic trapping. Condensation collection systems have been used with both diluted and raw vehicle exhausts. Figure 44 shows a condensation system for collecting POM from raw vehicle exhaust.[25] After initial filtration, the vehicle exhaust is condensed using cryogenic vessels cooled by water, dry ice/ethanol, or liquid nitrogen. Water and other condensable components of the exhaust are collected in the condensor and recovery flask. Both the condensate and the collected particulate are analyzed for POM.

Fugitive and Ambient Sampling

Sampling of POM in ambient air, and from specific fugitive emission sources has been described by several investigators.[26-29] Ambient and fugitive sampling procedures involve the collection of airborne particulate by means of filtration or impaction. Some methods combine filtration with adsorption techniques to ensure collection of vapor phase POM.

High volume samplers are the most commonly used device for collecting ambient particle-bound POM. These samples draw ambient air through a 20x25 cm glass fiber filter at rates of 1.1-1.7 cmm (40-60 cfm). Twenty-four hour sampling periods allow sample volumes of approximately 2039 cm (72,000 cf). An advantage in using high volume samplers is the large quantity of sample that can be collected in a day. Disadvantages are that the high flow rates and long sample periods can contribute to breakthrough of the more volatile POM as well as potentially contributing to the formation of artifacts.[30,31]

Low volume samplers, which operate at about one tenth the flow rate of high volumes, have been used by some investigators to collect particulate bound POM. Advantages in using low volume samplers are that breakthrough and artifact formation problems may be less important than with high volume samplers. The major disadvantage is the small sample size resulting from use of a low volume sampler. Small sample sizes limit the number and type of chemical analyses that can be performed.

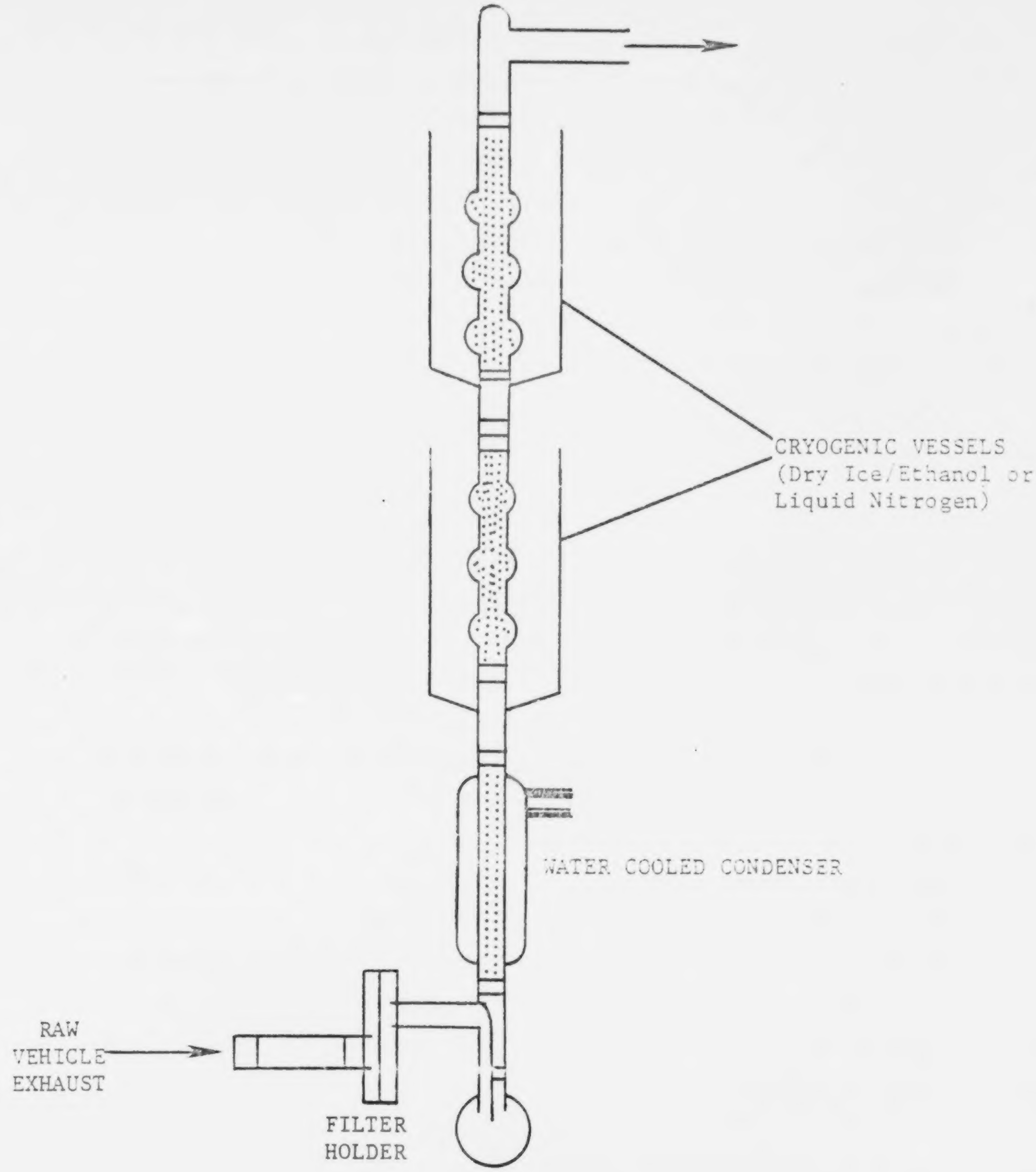

CRYOGENIC VESSELS
(Dry Ice/Ethanol or
Liquid Nitrogen)
WATER COOLED CONDENSER
RAW
VEHICLE
EXHAUST
FILTER
HOLDER

Figure 44. Condensation sampling system for raw vehicle exhaust.

The addition of adsorbent materials such as Tenax, Chromsorb 102, XAD-2, and polyurethane foam downstream of filtration or impaction devices have been described by some investigators.[32-34] These adsorbent materials collect breakthrough POM which evaporates from particulate during sample collection. In addition, these materials collect vapor phase POM that are typically not associated with particulate (e.g., compounds with less than four rings).

SAMPLE RECOVERY

Quantitative recovery of POM requires the separation of POM from the remainder of the collected material, as well as efficient removal from collection media. Solvent extraction techniques which are commonly used for recovery of POM from filters, adsorbent, and liquid media are briefly described.

Soxhlet

Soxhlet extraction is generally recognized as the standard method for preparing a POM-containing solvent extract of solid matrices.[34] This technique is applicable for the extraction of POM from both filter and sorbent catches. This procedure has been specified as a standard reference for extraction of POM by the American Society for Testing Materials, the U. S. Intersociety Committee on Recommended Methods, and the U. S. Environmental Protection Agency's Procedures Manual for Level 1 Environmental Assessment.[9,34]

Filter samples are folded and placed directly in the extraction chamber of the soxhlet. Polymeric resins are typically transferred to cellulose or glass extraction thimbles and then placed in the soxhlet for extraction. Recommended solvents and extraction periods vary depending on the sample matrix and the collection media.[35,36] Table 88 lists reported soxhlet extraction recoveries of POM from various sample matrices using a range of extraction periods and solvents.[35]

TABLE 88. SOXHLET EXTRACTION RECOVERIES OF POM FROM VARIOUS SAMPLE MATRICES[35]

Sample Matrix	POM[a]	Level[b]	Percentage Recovery[c]	Extraction Conditions	
				Solvent[d]	Time (hr)
Air particulates	BaP	4.57 ug	70 - 75[e]	CH	4
		1.96 ug	72 - 76[e]		
		0.37 ug	32 - 47[e]		
	3 - 5 ring	---	100	B or M	2 - 16
	BaP	1.12 mg/g	99 - 100	EA, A, EE, B/DEA	6
			95	B, MC, E	6
			76 - 77	C, H, T	6
			54	P	6
	BaP	100 ng	94 - 95	B	16
	4 - 6 ring	---	95 - 100	B	8
	5 - 6 ring	2 - 11 ug	"Complete"	B	6
Polyvinyl chloride smoke particles	2 - 5 ring	20 - 100 ug	90 - 104[e,f]	CH	2
"Environmental"	2 - 7 ring	---	40 - 88[e,f]	M then B	24 (each)
Coke oven particles	2 - 6 ring	---	99 - 100	B	2 - 4
Auto exhaust particles	BaP	---	61 - 85[e]	MC	14 - 16
	BaA	---	80	---	---
Coal fly ash	BaP	Radiotracer	18	B	64
	BaP	133 ug	60	B	32
	2 - 5 ring	90 - 250 ug	100	B	24
	4 - 6 ring	9.35 ug	32 - 91	MC	12
		31.7 ug	53 - 98	---	---

TABLE 88. SOXHLET EXTRACTION RECOVERIES OF POM FROM VARIOUS SAMPLE MATRICES[35] (Continued)

Sample Matrix	PAH[a]	Level[b]	Percentage Recovery[c]	Extraction Conditions	
				Solvent[d]	Time (hr)
River bottom sediment	Naphthalene	Radiotracer	100	A	68
	BaP	Radiotracer	100	A	68
	2 - 7 ring	---	86 - 89[e,f]	MC	12

[a] PAH used for recovery determination.

[b] Amount or concentration of PAH in recovery study.

[c] Extraction recovery, unless denoted otherwise.

[d] CH = cyclohexane; B = benzene; M = methanol; EA = ethyl acetate; A = acetone; T = toluene; P = pentane; DEA = diethyl amine; EE = diethyl ether; E = ethanol; MC = methylene chloride.

[e] Overall analytical recovery.

[f] Recovery may not include extraction.

Typical solvents used for extraction of POM from filters, include methylene chloride, cyclohexane, or benzene.[6,12,21,37] Some investigators recommend an initial extraction with methylene chloride followed by subsequent extraction with a more polar solvent such as methanol.[38] Solvents for extraction of polymeric resins are typically chosen based on the nature of the adsorbent. Methylene chloride followed by methanol is commonly selected for extracting POM from XAD-2 and Chromsorb 102 resins. Hydrocarbons, such as pentane followed by methanol, have been recommended for extracting Tenax.[39]

Sonication

Ultrasonic agitation or sonication uses high intensity ultrasonic vibration (~20 KHz) to enhance solvent sample contact. Extractions involve the insertion of a sonication probe into the sample-containing extraction vessel, or a sonication bath in which the sample-containing extraction vessel is set. Filter samples are typically shredded and placed in a glass extraction vessel along with solvents. Sonication is typically carried out for periods ranging from a few minutes to one hour.[40] Extracted POM are then separated from insoluble materials using conventional filtration techniques. Table 89 lists reported ultrasonic agitation recoveries of POM from air particulate and coal fly ash using a range of extraction periods and solvents.[41] Recommended solvents include cyclohexane, benzene, acetonitrile, tetrahydrofuran, and methylene chloride.[42]

Solvent Partitioning--

Solvent partitioning, or liquid-liquid extraction is the traditional procedure for extraction from liquid sample matrices.[9,43] The extraction is typically performed in a separatory funnel by agitation and shaking the sample-containing liquid with a suitable solvent. Reported solvents include methylene chloride and cyclohexane.[44]

TABLE 89. RECOVERIES OF POM FROM AIR PARTICULATE AND COAL FLY ASH BY ULTRASONIC EXTRACTION

Sample Matrix	POM[a]	Level[b]	Percentage Recovery	Extraction Conditions	
				Solvent[c]	Time
Air particulates	Anthr	35 mg	95	CH	8 min x 2
	Phen	147 ng	97.5		
	BaP	355 ng	98.2		
	BaP	---	$\geq$90	AN	5 min
	BaP	10 ug	46.5	B	5 min x 1
			70.4		5 min x 2
			83.1		5 min x 3
			91.0		5 min x 4
	BaP	200 ng	99.8	THF	10 min
	BaP	10 - 30 ug	96.6	CH	30 min x 1
			3.1		30 min x 2
			96.8		60 min x 1
			2.6		60 min x 2
Coal fly ash	BaP	100 ng/g	25.2	B	30 sec x 2

[a] Anthr = anthracene; BaP = benzo(a)pyrene; Phen = phenanthrene.

[b] Amount or concentration of POM in Recovery Study.

[c] AN = acetonitrile; CH = cyclohexane; B= benzene; THF = tetrahydrofuran.

IDENTIFICATION AND QUANTIFICATION OF POM

A variety of analytical techniques have been used to quantify the POM content of complex environmental samples. This section presents a brief overview of the most commonly used techniques.

High Performance Liquid Chromatography (HPLC)--

The use of liquid chromatography for the determination of specific POM compounds in complex environmental samples has increased significantly in recent years. Detailed reviews are available in the literature that describe various modes of separation, and applications of liquid chromatography (LC) in the measurement of POM.[45-52] Although not offering the high separation efficiency of capillary Gas Chromatography (GC), HPLC offers three distinct advantages for POM analysis. First, HPLC offers a variety of stationary and mobile phases which provide selectivity for the separation of POM isomers not generally separated by GC. Second, HPLC coupled with a fluorescence detector provides both sensitivity and selectivity. Individual POM compounds have characteristic fluorescence excitation and emission spectra, whereas isomeric POM have very similar if not identical mass spectra. Finally, HPLC is an extremely useful fractionation technique for the isolation of POM for subsequent analysis by other chromatographic or spectroscopic techniques.

Gas Chromatography (GC)--

Several studies have been performed using gas chromatography for the separation and determination of POM in environmental samples. Detailed reviews are available in the literature that describe various applications of GC.[53-56]

The most frequently used detector for GC analysis of POM is the flame ionization detector (FID). Its general response character makes it ideal for several classes of compounds, but necessitates an extensive clean-up procedure prior to GC to eliminate possible interfering compounds. The advantages of using FID include linear response, sensitivity, and day-to-day quantitative reliability to routine determinations. Typical detection limits are below 1 ng.

Numerous applications using the combination of Gas Chromatography and Mass Spectrometry (GC/MS) are also described. EPA Methods 625 and 1625 are both GC/MS techniques for the determination of POM compounds.[55,56] Advantages of GC/MS techniques include a high level of sensitivity for trace level detection, versatility for the separation of a large number of compounds, and specificity for absolute identification. The marked disadvantage is that it is significantly more expensive than other techniques.

REFERENCES FOR SECTION 5

1. Burlingame, J. D., et al. Field Test of Industrial Coal Stoker Fired Boilers for Inorganic Trace Element and Polynuclear Aromatic Hydrocarbon Emissions. EPA Report No. 600/7-81-167. U. S. Environmental Protection Agency, Research Triangle Park, Research Triangle Park, North Carolina. October 1981. p. 37.

2. Sonnichsen, T. W. Measurement of POM Emissions from Coal-fired Utility Boilers. EPRI Report No. CS-2885. Electric Power Research Institute, Palo Alto, California. February 1983. p. 3-1.

3. DeAngelis, D., D. Ruffin, and R. Reznik. Preliminary Characterization of Emissions from Wood-fired Residential Combustion Equipment. EPA Report No. 600/7-80-040. U. S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. March 1980.

4. Cottone, L. E. Summary Test Report of Test Method Evaluations and Emissions Testing for Rating Woodstoves. Prepared under EPA Contract No. 68-02-3996. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. December 1985. p. 2.

5. Jones, P. W., J. E. Wilkinson, and P. E. Strup. Measurement of Polycyclic Organic Materials and Other Hazardous Organic Compounds in Stack Gases, State of the Art. EPA Report No. 600/2-77-202. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1977. pp. 36-37.

6. Schlickenrieder, L. M., J. W. Adams, and K. E. Thrun. Modified Method 5 Train and Source Assessment Sampling System Operators Manual. Prepared under EPA Contract No. 68-02-3627. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. May 1984.

7. Reference 4, p. 14.

8. Reference 6, p. 1.

9. Lentzen, D. E., D. E. Wagoner, L. D. Estes, and W. F. Gutknecht. IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition. EPA Report No. 600/7-78-201. U. S. Environmental Protection Agency, Washington, D.C. October 1978.

10. Code of Federal Regulations, Title 40, Part 86, Particulate Regulation for Light-Duty Diesel Vehicles. Certification and Test Procedures. Thursday, February 1, 1979.

11. Code of Federal Regulations, Title 40, Gaseous Emission Regulations for 1984 and Later Model Year Heavy Duty Engines. January 21, 1980.

12. Lee, F. S., and D. Schuetzle. Sampling, Extraction, and Analysis of Polycyclic Aromatic Hydrocarbons from Internal Combustion Engines. In: Handbook of Polycyclic Aromatic Hydrocarbons, A. Bjorseth, ed. Marcel Dekker, Inc., New York. 1985. p. 30.

13. Stenberg, V. R. PAH Emissions from Automobiles. In: Handbook of Polycyclic Aromatic Hydrocarbons - Volume 2. A. Bjorseth and T. Ramdahl, eds. Marcel Dekker, Inc., New York. 1985. pp. 88-91.

14. Reference 13, p. 94.

15. Petersen, B. A., C. C. Chuang, T. L. Hayes, and D. A. Trayser. Analysis of PAH in Diesel Exhaust Particulate by High Resolution Capillary Column Gas Chromatography/Mass Spectrometry. In: Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry, Proceedings of the Sixth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1981. M. Cooke, A. J. Dennis, and G. L. Fisher, eds. Battelle Press, Columbus, Ohio. 1982. pp. 641-653.

16. Choudhury, D. R. and B. Bush. Polynuclear Aromatic Hydrocarbons in Diesel Emission Particulates. EPA Report No. 600/9-80-057a. W. E. Pepeko, R. M. Danner, and N. A. Clarke, eds. November 1980. pp. 175-185.

17. Hites, R. A., M. Yu, and W. G. Thilly. Compounds Associated with Diesel Exhaust Particulates. In: Polynuclear Aromatic Hydrocarbons: Chemical Analysis and Biological Fate, Proceedings of the Fifth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1980. M. Cooke and A. J. Dennis, eds. Battelle Press, Columbus, Ohio. 1981. pp. 455-466.

18. Warner-Selph, M. A., and H. E. Dietzmann. Characterization of Heavy-Duty Motor Vehicle Emissions Under Transient Driving Conditions, Project Summary. EPA Report No. 600/53-84-104. Atmospheric Sciences Research Laboratory, Research Triangle Park, North Carolina. December 1984. 6 pp.

19. Reference 12, p. 39.

20. Reference 13, p. 96.

21. Lee, F. S., T. J. Prater, and F. Fevris. PAH Emissions from a Stratified-Charge Vehicle With and Without Oxidation Catalyst: Sampling and Analysis Evaluation. In: Polynuclear Aromatic Hydrocarbons, Proceedings of the Third International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1978. P. W. Jones and P. Leber, eds. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan. 1979. pp. 83-110.

22. Reference 12, p. 41.

23. Reference 13, p. 98.

24. Reference 12, p. 40.

25. Reference 13, p. 97.

26. Chuang, C. C. and B. A. Petersen. Review of Sampling and Analysis Methodology for Polynuclear Aromatic Compounds in Air from Mobile Sources. EPA Report No. 600/4-85-045. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. June 1985. pp. 24-36.

27. White, C. M., A. G. Sharkey, M. L. Lee, and D. L. Vassilaros. Some Analytical Aspects of the Quantitative Determination of Polynuclear Aromatic Hydrocarbons in Fugitive Emissions from Coal Liquefication Processes. In: Polynuclear Aromatic Hydrocarbons, Proceedings of the Third International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1978. P. W. Jones and P. Leber, eds. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan. 1979. pp. 261-275.

28. Bjorseth, A. Determination of Polynuclear Aromatic Hydrocarbons in the Working Environment. In: Polynuclear Aromatic Hydrocarbons, Proceedings of the Third International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1978. P. W. Jones and P. Leber, eds. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan. 1979. pp. 371-381.

29. Engel, P. R. Ambient Air Monitoring Study of Residential Woodburning in Mio, Michigan. Presented at the 78th Annual Meeting of the Air Pollution Control Association, Detroit, Michigan. June 16-21, 1985. 85-43.2. 13 pp.

30. Reference 26, p. 28.

31. Lindskog, A. Transformation of Polycyclic Aromatic Hydrocarbons During Sampling. Environmental Health Perspectives. 47: 81-84. 1983.

32. Lindgren, J. L., H. J. Krauss, and M. A. Fox. A Comparison of Two Techniques for the Collection and Analysis of Polynuclear Aromatic Compounds in Ambient Air. Journal of the Air Pollution Control Association. 30(2): 166-168. 1980.

33. Keller, C. D., and T. F. Bidleman. Collection of Airborne Polycyclic Aromatic Hydrocarbons and Other Organics with a Glass Fiber Filter Polyurethane Foam System. Atmospheric Environmental. 18: 837-845. 1984.

34. Griest, W. H., and J. E. Caton. Extraction of Polycyclic Aromatic Hydrocarbons for Quantitative Analysis. In: Handbook of Polycyclic Aromatic Hydrocarbons, A. Bjorseth, ed. Marcel Dekker, Inc., New York. 1983. p. 99.

35. Reference 34, pp. 102-103.

36. Reference 12, p. 45.

37. Reference 34, pp. 102-104.

38. Reference 5, pp. 41-43.

39. Reference 5, p. 42.

40. Reference 34, p. 107.

41. Reference 34, p. 108.

42. Reference 34, pp. 107-112.

43. Reference 34, p. 112.

44. Reference 34, p. 114.

45. Dong, M. W., K. Ogan, and J. L. DiCesare. Very High-Speed Liquid Chromatography for PAH Analysis System and Applications. In: Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry, Proceedings of the Sixth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1981. M. Cooke, A. J. Dennis, and G. L. Fisher, eds. Battelle Press, Columbus, Ohio. 1982. pp. 237-245.

46. Wise, S. A. Recent Progress in the Determination of PAH by High Performance Liquid Chromatography. In: Handbook of Polycyclic Aromatic Hydrocarbons, A. Bjorseth and T. Ramdahl, eds. Marcel Dekker Inc., New York. 1985. p. 113.

47. May, W. E., S. A. Wise. Liquid Chromatographic Determination of Polycyclic Aromatic Hydrocarbons in Air Particulate Extracts. Analytical Chemistry. 56: 225-232.

48. Zelenski, S. G., G. T. Hunt, and N. Pangaro. Comparison of SIM GC/MS and HPLC for the Detection of Polynuclear Aromatic Hydrocarbons in Fly Ash Collected from Stationary Sources. In: Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Proceedings of the Fourth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1979. A. Bjorseth and A. J. Dennis, eds. Battelle Press, Columbus, Ohio. 1980. pp. 589-597.

49. Vandemark, F. L., and J. L. DiCesare. The Application of High Resolution Preparative Liquid Chromatography to the Polycyclic Aromatic Hydrocarbons. In: Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry, Proceedings of the Sixth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1981. M. Cooke and A. J. Dennis, and G. L. Fisher, eds. Battelle Press, Columbus, Ohio. 1982. pp. 835-843.

50. James, R. H., R. E. Adams, J. M. Finkel, H. C. Miller, and L. D. Johnson. Evaluation of Analytical Methods for the Determination of POHC in Combustion Products. Journal of the Air Pollution Control Association. 35(9): 959-969. September 1985.

51. Wise, S. A. High-Performance Liquid Chromatography for the Determination of Polycyclic Aromatic Hydrocarbons. In: Handbook of Polycyclic Aromatic Hydrocarbons, A. Bjorseth, ed. Marcel Dekker, Inc., New York. 1983. p. 183.

52. Federal Register, Volume 49, No. 209. Method 610 Polynuclear Aromatic Hydrocarbons. pp. 112-120.

53. Bartle, K. S. Recent Advances in the Analysis of Polycyclic Aromatic Compounds by Gas Chromatography. In: Handbook of Polycyclic Aromatic Hydrocarbons - Volume 2, A. Bjorseth and T. Ramdahl, eds. Marcel Dekker, Inc. New York. 1985. pp. 193-237.

54. Reference 26, pp. 37-58.

55. Federal Register, Volume 49, No. 209. October 26, 1984. Method 1625 Revision B Organic Compounds by Isotopic Dilution GC/MS. pp. 184-197.

56. Federal Register, Volume 49, No. 209. October 26, 1984. Method 625 - Base/Neutrals and Acids. pp. 153-174.